ACS SYMPOSIUM SERIES 1072

Understanding Greenhouse Gas Emissions from Agricultural Management

EDITED BY
Lei Guo, Amrith S. Gunasekara,
and Laura L. McConnell

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.fw001

Understanding Greenhouse Gas Emissions from Agricultural Management

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.fw001

ACS SYMPOSIUM SERIES **1072**

Understanding Greenhouse Gas Emissions from Agricultural Management

Lei Guo, Editor
California Air Resources Board
Sacramento, California

Amrith S. Gunasekara, Editor
California Department of Food and Agriculture
Sacramento, California

Laura L. McConnell, Editor
Agriculture Research Service
U.S. Department of Agriculture
Beltsville, Maryland

Sponsored by the
ACS Division of Agrochemicals

American Chemical Society, Washington, DC

Distributed in print by Oxford University Press, Inc.

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.fw001

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.fw001

Library of Congress Cataloging-in-Publication Data

Library of Congress Cataloging-in-Publication Data

Understanding greenhouse gas emissions from agricultural management / Lei Guo, Amrith S. Gunasekara, Laura L. McConnell, editor[s] ; sponsored by the ACS Division of Agrochemicals.
p. cm. -- (ACS symposium series ; 1072)
Includes bibliographical references and index.
ISBN 978-0-8412-2654-8 (alk. paper)
1. Agricultural pollution--Congresses. 2. Soil pollution--Congresses. 3. Farm management--Environmental aspects--Congresses. 4. Greenhouse gases--Congresses. I. Guo, Lei, 1959- II. Gunasekara, Amrith S. III. McConnell, Laura L. IV. American Chemical Society. Division of Agrochemicals.
TD195.A34U53 2011
363.738′74--dc23
2011033453

The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences—Permanence of Paper for Printed Library Materials, ANSI Z39.48n1984.

Copyright © 2011 American Chemical Society

Distributed in print by Oxford University Press, Inc.

All Rights Reserved. Reprographic copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Act is allowed for internal use only, provided that a per-chapter fee of $40.25 plus $0.75 per page is paid to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. Republication or reproduction for sale of pages in this book is permitted only under license from ACS. Direct these and other permission requests to ACS Copyright Office, Publications Division, 1155 16th Street, N.W., Washington, DC 20036.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

PRINTED IN THE UNITED STATES OF AMERICA

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.fw001

Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

ACS Books Department

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.pr001

Preface

Global warming, caused predominantly by the accumulation of greenhouse gases (GHGs), such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), in the atmosphere, is one of the greatest challenges facing humanity in the 21st century. There is compelling evidence that the earth is warming at an unprecedented rate. The past century has witnessed significant global temperature rise, glacial retreat, sea level rise, ocean acidification and increases in extreme weather events such as flooding, drought and wildfire.

Since the birth of the United Nations Framework Convention on Climate Change (UNFCCC) in 1992, and the subsequent adoption of its Kyoto Protocol in 1997, over 190 countries and nations, as well as many state entities in the United States have realized the urgency of curbing GHG emissions in an effort to combat global warming. In California, for example, an Assembly Bill titled "the California Global Warming Solutions Act of 2006," or AB 32, was enacted which mandates the reduction of statewide GHG emissions to 1990 levels by 2020. As part of a coordinated scientific research on GHG emissions from agricultural sources, the largest contributor of global anthropogenic CH_4 and N_2O, we hosted a symposium to understand baseline measurements, mitigation strategies and modeling efforts of GHGs from managed agriculture systems at the American Chemical Society's Spring 2010 National Meeting, held in San Francisco, California. This book highlights some of the research presented at the symposium and includes also chapters contributed by other lead scientists around the world who were unable to participate in the symposium.

The book is divided into three sections. Section 1, Field Study of Greenhouse Gas Emissions and Mitigation in Agricultural Cropping Systems, focuses on baseline and mitigation potentials of GHG emissions from agricultural fields. The chapters cover a wide range of technical issues on emission measurement methodologies, inventory development, effects of environmental variables on emissions, and potential mitigation strategies and control technologies. Climate impacts of aerosols from agricultural burning are also discussed. Section 2, Modeling of Greenhouse Gas Emissions and Mitigation in Agricultural Cropping Systems, introduces the two leading geochemical models, DeNitrification-DeComposition (DNDC) and DayCent, used for assessing GHG emissions in agricultural land uses. The chapters illustrate the structure and basic components of the models, and demonstrate the power and role of the modeling approach as a cost-effective tool in assessing GHG emissions from complicated agroecosystems. The last Section, Greenhouse Gas Emissions and Mitigation in Animal Systems, reviews GHG emissions from the livestock industry and discusses effects of various animal operations on GHG emissions, including animal breeding, animal housing and feeding options, waste treatment and storage methods, and land application of animal wastes. Emission estimates are provided for major types of livestock animals. With its broad perspectives, the book is intended for a wide audience in both scientific communities and the general public. It is our hope that this book can not only provide a comprehensive review on the issues related to agricultural GHGs for the researchers, but also raise the awareness of the general public about global warming, one of the most important and pressing concerns of our times.

We are extremely grateful to the authors of this book who have dedicated tremendous time and efforts amid their already tight teaching and research schedule to make this book possible. Our gratitude is also extended to the reviewers whose scientific insights and feedbacks were crucial in ensuring the high quality of this book. We appreciate the American Chemical Society for providing such a venue for bringing together scientists and stakeholders worldwide to discuss environmental concerns and explore potential solutions. Finally, we would like to express our sincere thanks to the agencies of California Air Resources Board, California Department of Food and Agriculture and United States Department of Agriculture, Agricultural Research Service for allowing us the freedom to pursue and complete this important project.

Lei Guo, Ph.D.
California Air Resources Board
Sacramento, California

Amrith S. Gunasekara, Ph.D.
California Department of Food and Agriculture
Sacramento, California

Laura L. McConnell, Ph.D.
Agricultural Research Service
United States Department of Agriculture
Beltsville, Maryland

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.pr001

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

Chapter 1

Quantifying Nitrous Oxide Emissions from Agricultural Soils and Management Impacts

S. J. Del Grosso*,1,2 and W. J. Parton[2]

[1]USDA, Agricultural Research Service, 2150 Centre Ave, Bldg. D, Ste. 100,
Fort Collins, CO 80526
[2]Natural Resource Ecology Laboratory, Colorado State University,
1231 East Drive, Fort Collins, CO 80526
*E-mail: Steve.delgrosso@ars.usda.gov

Nitrous oxide (N_2O) is the primary greenhouse gas associated with most non-flooded cropping systems. N_2O emissions have been measured from numerous experimental plots around the world; most often using ground based chambers but recently estimates based on top down approaches have become available. Data resulting from these measurements led to the development of N_2O emission models of varying complexity. Comparing N_2O fluxes estimated by different methods shows that as scale increases, estimates based on different modeling and measuring approaches tend to converge. As scale decreases, complex models that simulate the plant-soil system usually agree more closely with measurements than simple models that are based on regression equations. Because about 25-50% of the N fertilizer added to soils is typically lost from the plant-soil system, there is potential to reduce N_2O emissions with improved management. Promising technologies include N fertilizers with urease and nitrification inhibitors and time released fertilizers. At the farm level, complex models appear to be the best method to quantify the management impacts on emissions because extensive measuring is too expensive and simple models are not reliable at this scale. But the ability of the models to represent how available land management options interact with environmental conditions to control soil greenhouse gas emissions is incomplete and further model development and testing are required. In particular, model outputs need to

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

be compared with observations of N_2O emissions and other nitrogen and carbon fluxes at various spatial and temporal scales.

Introduction

Nitrous oxide (N_2O) is an important greenhouse gas with a Global Warming Potential (GWP) approximately 300 times that of carbon dioxide (CO_2). With the decline of chlorofluorocarbon emissions resulting from the Montreal Protocol, N_2O is now thought to be the dominant stratospheric ozone depleting substance (*1*). Agriculture is responsible for the majority of anthropogenic N_2O emissions in the US (*2*) and globally (*3*). Burning of crop residues and manure management systems contribute to N_2O emissions but the biggest source is cropped and grazed soils. The microbial processes of nitrification and denitrification are responsible for soil N_2O emissions. Nitrification is the oxidation of ammonium to nitrate while denitrification is the reduction of nitrate to N_2O, as well as N_2 (These and other soil processes are described in detail in Chapter 17 of this volume). Both nitrification and denitrification occur naturally in soils but common agricultural practices tend to enhance their rates and cause emissions from managed soils to exceed background rates. In particular, nitrogen (N) inputs from fertilizer and manure amendments and cropping of N fixing legumes influence soil N cycling and provide substrates for nitrification and denitrification. Although the biochemistry of these processes has been studied for decades, there remains a fair amount of uncertainty in estimates of N_2O emissions from agro-ecosystems. In this chapter we discuss the different methods to quantify N_2O emissions and their uncertainties, and technologies to reduce emissions and increase N use efficiency.

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

Methods to Quantify N_2O Emissions

Methods to quantify N_2O emissions can be placed into two broad categories, those based on measurements and those based on models. Measuring methods are further partitioned into bottom up and top down methods. Bottom up methods involve placing air tight chambers on ‘anchors’ driven into the soil (Figure 1). Changes in gas concentration measured immediately upon chamber placement and at successive time intervals (e.g., 0, 15, and 30 minutes after chamber placement) are used to infer instantaneous gas flux. Chamber methodology was developed decades ago and is responsible for the majority of soil N_2O flux observations. Chambers provide snapshots of emissions at fine temporal and spatial resolution and are appropriate for plot level studies. However, disturbance of vegetation and soil are required and because spatial and temporal variability of N_2O fluxes are high, sufficient sampling frequency and spatial coverage of anchors are required. Studies comparing measurements from automated chambers (several measuring periods per day) with manual measurements of different frequencies suggest that measuring frequency should be at least once per week to ensure reasonable agreement with results from more intensive sampling (*4*, *5*).

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

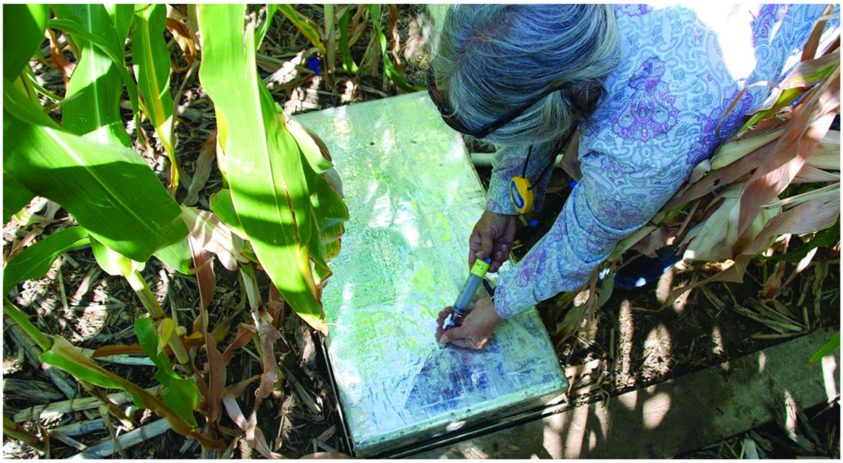


Figure 1. Ground level chamber method for measuring soil surface trace gas flux.

Top down methods do not appreciably disturb the system and have a larger spatial footprint than chambers. The eddy covariance method originally developed to measure land surface CO_2 and H_2O vapor fluxes have recently been adapted for N_2O (Figure 2). Continuous monitoring of N_2O concentration and vertical wind speed at a given height (e.g., 3 meters) above the surface are used to calculate gas flux at small time intervals (e.g., 15 minutes). The spatial foot print is a function of instrument height and horizontal wind speed. This method is appropriate for the field scale and provides almost continuous sampling through time. However, it cannot distinguish emissions from plots receiving different treatments and is impacted by wind velocity. In particular, low night time vertical mixing precludes accurate measurements of night time fluxes. Tower-based systems have similar advantages and disadvantages of eddy covariance methods but use the flux gradient technique (*6*). N_2O measured from instruments placed at different heights (e.g., 3 m and 2 m) and wind velocity measurements are used to calculate flux rates.

Aircraft-mounted gas concentration and wind velocity sensors have also recently been used to monitor N_2O fluxes over even larger scales using the eddy covariance method (*7*). Disadvantages of this method include expense and limited temporal coverage, since measurements can be made only for discrete time periods. The global top down method estimates N_2O emissions based on measurements of atmospheric concentration of N_2O through time and estimates of the photochemical sink strength in the stratosphere (*8*). This method integrates over the entire globe and thus cannot be used for greenhouse gas source attribution, but does provide a constraint for global estimates scaled up by using other methods.

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

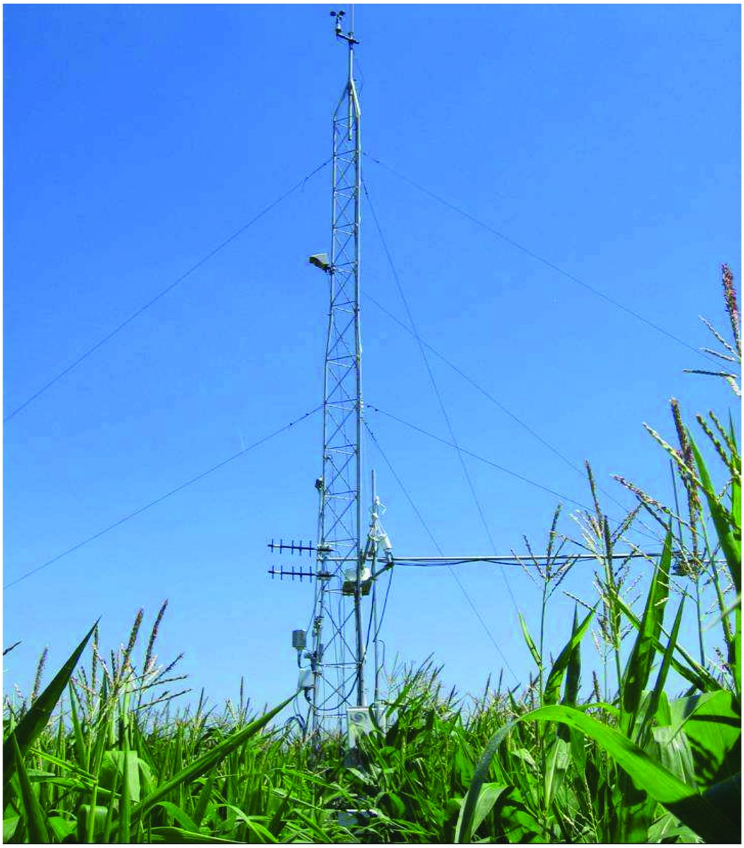


Figure 2. Flux tower for measuring trace gas flux from the plant-soil system.

Models used to quantify soil surface N_2O emissions range from simple empirical equations to complex models that simulate the processes that control emissions. The most commonly used empirical method is the Tier 1 Intergovernmental Panel on Climate Change (IPCC) emission factor approach which assumes that 1% of N applied to soil from different sources (e.g., fertilizer amendments, crop residues) is emitted as N_2O-N on an annual basis (*9*). This method is simple to apply and calculations are highly transparent but the uncertainty range is large (-70% to +200%). Models that simulate important processes in the plant-soil system (e.g., soil water and heat fluxes, net primary productivity, biomass senescence and harvest, organic matter decomposition, nutrient mineralization, nitrification, denitrification) usually have smaller uncertainty ranges but results are not highly transparent and more complex input data as well as sufficient computing resources are required.

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

DayCent (Daily Century) is a process based model of intermediate complexity widely used to estimate soil N_2O emissions and other flows of carbon and nutrients. DayCent is the daily time step version of the CENTURY model (*10*). CENTURY was developed in the 1970's to simulate changes in plant growth, soil organic matter cycling, and other ecosystem factors in response to changes in land management and climate (*11*). CENTURY operates at a monthly time step, which is adequate to model plant growth and soil organic matter changes. However, finer resolution is required to simulate soil trace gas (N_2O, NO_x, CH_4) fluxes. DayCent uses readily available inputs and has the ability to simulate common disturbance and management events (e.g., fire, grazing, cultivation, harvest, irrigation, fertilization).

DayCent simulates exchanges of carbon, nutrients, and trace gases among the atmosphere, soil, and plants (Figure 3). Required model inputs are: soil texture, current and historical land use, and daily maximum/minimum temperature and precipitation data. Plant growth is a function of soil nutrient and water availability, temperature, and plant specific parameters such as maximum growth rate, minimum and maximum biomass carbon to nutrient ratios, and above vs. below ground carbon allocation. Soil carbon levels fluctuate according to inputs from senesced biomass (after accounting for biomass removal during harvest operations and disturbance events) and manure amendments, as well as losses from microbial respiration. Nitrogen gas (N_2O, NO_x, N_2) emissions from nitrification and denitrification are controlled by soil mineral N (nitrate and ammonium) levels, water content, temperature, pH, plant N demand, and labile C availability. Nitrate leaching losses are controlled by soil NO_3 availability, saturated hydraulic conductivity, and water inputs from rainfall, snowmelt, and irrigation.

The ability of DayCent to simulate crop yields, soil organic matter, N_2O emissions, and nitrate (NO_3) leaching has been validated by comparing model outputs with measurements from various cropped and grassland systems in North America (*12–14*). DayCent has been applied to simulate soil greenhouse gas fluxes at scales ranging from plots to regions to the globe (*10*, *12*, *15*). The model has been used since 2005 to calculate N_2O emissions from agricultural soils for the U.S. National Greenhouse Gas Inventory complied by the Environmental Protection Agency (EPA) and reported annually to the United Nations Framework Convention on Climate Change (*2*, *16*). Some model limitations include: not accounting for the influence of topography on lateral water and nutrient flows, ammonium (NH_4) is considered to be immobile and is confined to the top 15 cm soil layer, and the impacts of microbial community diversity on biochemical processes are discounted.

With recent technological advances (i.e. increased access to databases with needed model driver data and development of user friendly interfaces) it is becoming easier for non-experts to use complex simulation models to estimate emissions (e.g., (*17*)). The COMET-VR_2.0 – Decision Support System for Agricultural Greenhouse Gas Accounting is designed to be used by land managers and is freely available (http://www.comet2.colostate.edu/). The package is easy to use and conducts DayCent simulations to quantify greenhouse gas emissions as well as uncertainty intervals.

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

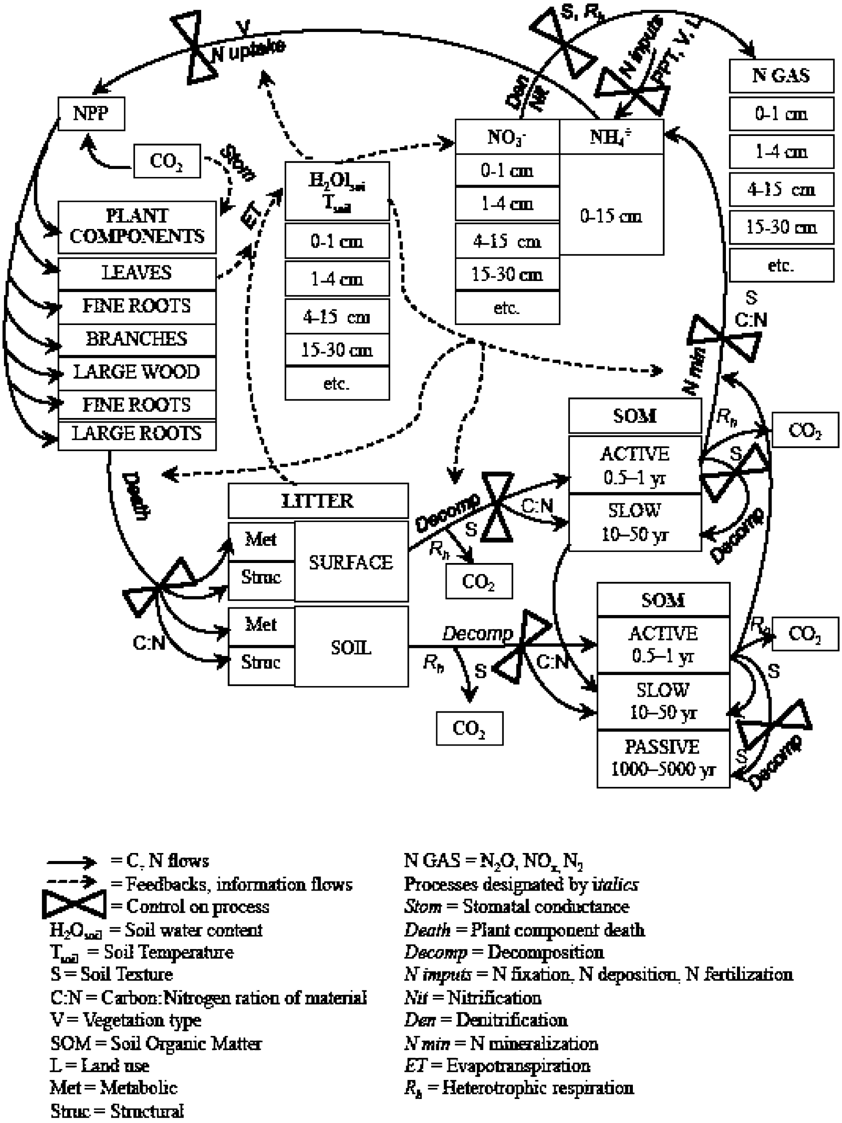

V
N uptake
S, R_h
N inputs
PPT, V, L
Den
Nit
N GAS
0-1 cm
1-4 cm
4-15 cm
15-30 cm
etc.
NPP
CO_2
Stom
ET
H_2O_{soil}
T_{soil}
0-1 cm
1-4 cm
4-15 cm
15-30 cm
etc.
NO_3^-
NH_4^+
0-1 cm
1-4 cm
4-15 cm
15-30 cm
etc.
0-15 cm
PLANT COMPONENTS
LEAVES
FINE ROOTS
BRANCHES
LARGE WOOD
FINE ROOTS
LARGE ROOTS
S
C:N
N min
SOM
ACTIVE 0.5–1 yr
SLOW 10–50 yr
R_h
CO_2
S
Decomp
Death
LITTER
Met
Struc
SURFACE
Met
Struc
SOIL
Decomp
C:N
S
R_h
CO_2
C:N
Decomp
R_h
S
CO_2
C:N
SOM
ACTIVE 0.5–1 yr
SLOW 10–50 yr
PASSIVE 1000–5000 yr
R_h
CO_2
S
S
Decomp
= C, N flows
= Feedbacks, information flows
= Control on process
H_2O_{soil} = Soil water content
T_{soil} = Soil Temperature
S = Soil Texture
C:N = Carbon:Nitrogen ration of material
V = Vegetation type
SOM = Soil Organic Matter
L = Land use
Met = Metabolic
Struc = Structural
N GAS = N_2O, NO_x, N_2
Processes designated by *italics*
Stom = Stomatal conductance
Death = Plant component death
Decomp = Decomposition
N inputs = N fixation, N deposition, N fertilization
Nit = Nitrification
Den = Denitrification
N min = N mineralization
ET = Evapotranspiration
R_h = Heterotrophic respiration

Figure 3. Flow diagram for the DayCent biogeochemical model.

Uncertainties and Comparisons of Methods

There are pros, cons, and uncertainties associated with all available methods to quantify soil N_2O emissions. Measurements represent our best estimate of ‘truth’ but it is prohibitively expensive to achieve complete spatial and temporal coverage and measuring methods often disturb the system. Models do not alter the system and can provide more complete spatial and temporal coverage, but are simplifications of reality. It is thus important to compare estimates using the different methods to better inform these strengths and weaknesses and to improve uncertainty assessments.

It has long been recognized that N_2O emissions are highly variable in space and time, uncertainty in both measured and modeled estimates can be quite high, and coefficients of variation (CV) for measured N_2O can exceed 100% (e.g. (*18*)). But recent improvements in methodologies and instrumentation have narrowed the uncertainties and CV for daily measurements are often less than 50% (e.g. (*19–21*)). Improvements in uncertainties have also been recently achieved for model generated estimates of emissions. Del Grosso et al. (*10*) developed a methodology to rigorously account for both uncertainty in model inputs and model structure. Probability distribution functions were developed for model inputs and a series of Monte Carlo simulations were conducted to assess uncertainty due to lack of precise input data. But even if inputs were precisely known, there is still error due to model structure because the algorithms and parameters in the model are imperfect representations of reality. A statistical equation was derived by comparing model outputs with measured emissions from experiments in North America to quantify model structural uncertainty. The calculated uncertainty for N_2O emissions for cropped soils in the US using this method (-33% to +50%) is smaller than previous estimates ranging from -70% to +184% (*22*) to +/- 57% (*23*).

Uncertainties in soil N_2O emissions can also be addressed by comparing estimates derived from different methods. Nitrous oxide measured from forests in Finland and Denmark using eddy covariance was found to agree well with ground based chamber measurements (*24*). Flux tower and aircraft based measurements of N_2O from an agricultural area in eastern Canada showed good agreement after accounting for differences in footprint sizes and landscape make up. Nitrous oxide emissions from agriculture calculated using the Tier 1 IPCC (2006) methodology agreed surprisingly well with emissions calculated using a top-down approach (*8*) at the global scale (*25*). Both methods estimated that about 4% of newly fixed N from fertilizer production and legume cultivation is emitted as N_2O-N from agricultural production systems. Although the default IPCC emission factor is only 1% for N from fertilizer and managed manure added to soils, this factor also applies to N in unharvested crop residue; also, the emission factor is 2% for N in unmanaged manure deposited onto soil by grazing livestock. Additionally, the IPCC method includes N_2O from the following sources: indirect N_2O resulting from N that left the farm in a form other than N_2O (e.g., volatilized NH_3, leached NO_3) and was converted to N_2O offsite, and N_2O from manure management systems. When all of these sources of N_2O are considered from a life cycle perspective, approximately 4% of newly fixed N from fertilizer production and legume fixation is assumed to be converted to N_2O and released into the atmosphere. A general pattern is that as scale increases, different methods of calculating emissions tend to converge (*25*). Similarly, model outputs for N_2O emissions often show poor agreement with observations at the daily scale, but good agreement when emissions are aggregated to seasonal or annual values (*7*) and model uncertainty tends to decrease as scale increases (*10*).

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

Nitrous Oxide Mitigation

Approximately 50-75% of N inputs to crops from fertilizer amendments and fixation are typically removed during harvest (*26*) thus, there is an opportunity to increase N use efficiency while decreasing N_2O emissions and other N loss pathways. The primary reason for these losses is that N availability is not entirely synchronous with plant N demand so at least during some time periods, N is in excess. This excess N is eligible to be leached below the rooting zone during sufficiently intense rainfall events and can be converted to gaseous compounds by soil biochemical processes and lost from the plant-soil system. In contrast, native systems that are not fertilized are more N limited and rarely experience conditions when N availability greatly exceeds plant N demand. This is because N is gradually released in small amounts during decomposition of soil organic matter and dead plant material. In sum, the N cycle is much tighter in native systems and usually less than 10% of the N that cycles is lost on an annual basis. Thus, the challenge is to make managed systems more like native systems in that excess N is minimized, while at the same time ensuring that available N is sufficient to satisfy plant demand.

Strategies to reduce N losses include application of nitrification and urease inhibitors, time released fertilizer, timing fertilizer application events to be more synchronous with plant N demand, strategically placing fertilizer in the rooting zone instead of uniformly across the soil surface, and reducing the amount of N fertilizer applied. When evaluating these mitigation options, results should be presented per unit of product. For example, greatly reducing N fertilizer additions would reduce emissions substantially on a unit area basis but yields would likely decrease as well, thus necessitating an increase in the amount of cropped land to keep total yield constant. It should also be noted that since the early 1980’s, the amount of fertilizer applied to US crops has increased by only ~20%, but crop yields have almost doubled (*27*). To help continue these N use efficiency gains the ‘4 rights’ regarding fertilizer application are advocated: apply the right product, at the right rate, during the right time, and at the right place (*28*). The right product is often ammonium instead of nitrate based, and includes nitrification and urease inhibitors, or polycoated urea. The right rate is based on soil N availability and yield goals. The right time is usually during the beginning of the growing season and the right place is often below the soil surface or banded on the surface so that more fertilizer intersects plant roots.

Practicing the ‘4 rights’ outlined above minimizes N losses during the growing season but non growing season losses can still be substantial. If unexpected weather events result in lower yields than anticipated, then at least a portion of the excess N that was not taken up by plants and harvested is likely to be lost during the non-growing season. Even when yields meet or exceed expectations, decomposition of unharvested plant residues and soil organic matter mineralizes N that can then be lost via leaching or gaseous emissions. An effective way to minimize these N losses is to grow winter season cover crops to scavenge excess N (*29*). However, cover crops are often not profitable for farmers so incentives are usually needed to encourage cover crop adoption. In addition to N losses, we also advocate accounting for the impacts of different management alternatives on other greenhouse gas fluxes (CO_2, CH_4). The economic costs/benefits of different alternatives, as well as the potential incentives, also need to be considered.

Programs to incentivize improved N management require methods to assess the reduction in emissions achieved under different management options. However, it is not feasible to sample individual farms at the required intensity to accurately determine N_2O emissions. Default Tier 1 IPCC methodology (*9*) provides reasonable estimates of N_2O emissions at large scales and can be used to estimate emissions at the farm level, but evidence shows that this methodology is often not reliable at the experimental plot level (*25*). This suggests that default Tier 1 methodology is also not reliable at the farm level. Complex models account for site level impacts not included in the default Tier 1 methodology and have been shown to be reasonably reliable at the plot scale, and are expected to be more reliable than default Tier 1 methodology at the farm level. Recent improvements in computing hardware and software development now facilitate the use of farm level decision support tools such as the COMET tool discussed above. However, current tools are limited in that they do not adequately represent all of the currently available mitigation technologies and have been tested for only a limited number of cropping systems. For example, the DayCent model, which is used to calculate N_2O emissions in the COMET tool, does not realistically simulate the impacts of fertilizer placement, and has only been extensively tested for major commodity crops. To increase confidence in tools such as COMET, model outputs need to be compared with observations of N_2O emissions and other nitrogen and carbon fluxes at various spatial and temporal scales. Fortunately, data sets that include measurements of N and C fluxes, as well as model driver data, are becoming increasingly available.

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

Conclusion

Nitrous oxide emissions are difficult to quantify using measurements because variability in space and time is high. It is also difficult to model emissions because various factors interact, often non-linearly, to control emissions. But recent advances in measuring and modeling technologies have significantly improved emission estimates and future estimates should be even more reliable. Better quantification of the temporal and spatial variability in emissions and improvement of mitigation technologies allow incentive programs to identify region and farm level specific best management practices that limit the release of N_2O and other greenhouse gases while maintaining high crop and forage yields.

References

1. Ravishankara, A. R.; Daniel, J. S.; Portmann, R. W. Nitrous oxide (N_2O): the dominant ozone-depleting substance emitted in the 21st century. *Science* **2009**, *326*, 123–125.
2. EPA. *Inventory of US greenhouse gas emissions and sinks: 1990-2009*; Environmental Protection Agency, Office of Atmospheric Programs: Washington, D.C., 2011

3. Smith, K. *Nitrous oxide and climate change*; Earthscan: London, United Kingdom and Washington, D.C., USA. 2010; Chapter 1, pp 1−3.
4. Parkin, T. B. Effect of sampling frequency on estimates of cumulative nitrous oxide emissions. *J. Environ. Qual.* **2008**, *37*, 1390–1395.
5. Smith, K. A.; Dobbie, K. E. The impact of sampling frequency and sampling times on chamber-based measurements of N_2O emissions from fertilized soils. *Global Change Biol.* **2001**, *7*, 933–945.
6. Pattey, E.; Edwards, G.; Strachan, I. B.; Desjardins, R. L.; Kaharabata, S.; Wagner Riddle, C. Towards standards for measuring greenhouse gas flux from agricultural fields using instrumented towers. *Can. J. Soil Sci.* **2006**, *86*, 373–400.
7. Desjardins, R. L.; Pattey, E.; Smith, W. N.; Worth, D.; Grant, B.; Srinivasan, R.; MacPherson, J. I.; Mauder, M. Multiscale estimates of N_2O emissions from agricultural lands. *Agric. For. Meteorol.* **2010**, *150*, 817–824.
8. Crutzen, P . J.; Mosier, A. R.; Smith, K. A.; Winiwarter, W. N_2O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmos. Chem. Phys.* **2008**, *8* (2), 389–395.
9. IPCC. *Intergovernmental Panel on Climate Change Guidelines for National Greenhouse Gas Inventories. Volume 4: Agriculture, Forestry and Other Land Use*; N_2O Emissions from Managed Soils, and CO_2 Emissions from Lime and Urea Application. 2006; Chapter 11.
10. Del Grosso, S. J.; Ogle, S. M.; Parton, W. J.; Breidt, F. J. Estimating uncertainty in N_2O emissions from US cropland soils. *Global Biogeochem. Cycles* **2010**, *24*, GB1009.
11. Parton, W. J.; Ojima, D. S.; Cole, C. V.; Schimel, D. S. A general model for soil organic matter dynamics: sensitivity to litter chemistry, texture and management. In *Quantitative Modeling of Soil Forming Processes*; SSSA, Spec. Pub. 39, Madison, WI, 1994; p 147−167.
12. Del Grosso, S. J.; Mosier, A. R.; Parton, W. J.; Ojima, D. S. DAYCENT model analysis of past and contemporary soil N_2O and net greenhouse gas flux for major crops in the USA. *Soil Tillage Res.* **2005**, *83*, 9–24.
13. Del Grosso, S. J.; Parton, W. J.; Ojima, D. S.; Keough, C. A.; Riley, T. H.; Mosier, A. R.. DAYCENT Simulated effects of land use and climate on county level N loss vectors in the USA. In *Nitrogen in the Environment: Sources, Problems, and Management*; Follett, R. F., Hatfield, J. L., Eds.; Elsevier: Amsterdam, The Netherlands, 2008; p 571−595.
14. Del Grosso, S. J.; Halvorson, A. D.; Parton, W. J. Testing DAYCENT model simulations of corn yields and nitrous oxide emissions in irrigated tillage systems in Colorado. *J. Environ. Qual.* **2008**, *37*, 1383–1389.
15. Del Grosso, S. J.; Ojima, D. S.; Parton, W. J.; Stehfest, E.; Heistemann, M.; Deangelo, B.; Rose, S. Global scale DAYCENT model analysis of greenhouse gas mitigation strategies for cropped soils. *Global Planet. Change* **2009**, *67*, 44–50.
16. Del Grosso, S. J.; Parton, W. J.; Mosier, A. R.; Walsh, M. K.; Ojima, D. S.; Thornton, P. E. DAYCENT national scale simulations of N_2O emissions from cropped soils in the USA. *J. Environ. Qual.* **2006**, *35*, 1451–1460.

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

17. Paustian, K.; Brenner, J.; Easter, M.; Killian, K.; Ogle, S.; Olson, C.; Schuler, J.; Vining, R.; Williams, S. Counting carbon on the farm: reaping the benefits of carbon offset programs. *J. Soil Water Conserv.* **2009**, *64*, 36A–40A.
18. Mosier, A.; Schimel, D; Valentine, D.; Bronson, K.; Parton, W. Methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands. *Nature* **1991**, *350*, 330–332.
19. Almaraz, J. J.; Mabood, F.; Zhou, X.; Madramootoo, C.; Rochette, P.; Smith, D. L. Carbon dioxide and nitrous oxide fluxes in corn grown under two tillage systems in Southwestern Quebec. *Soil Sci. Soc. Am. J.* **2009**, *73*, 113–119.
20. Wolf, B.; Zheng, X.; Brüggermann, N.; Chen, W.; Dannenmann, M.; Han, X.; Sutton, M. A.; Wu, H.; Yao, Z.; Butterbach-Bahl, K. Grazing-induced reduction of natural nitrous oxide release from continental steppe. *Nature* **2010**, *464*, 881–884.
21. Halvorson, A. D.; Del Grosso, S. J.; Alluvione, F. Tillage and inorganic nitrogen source effects on nitrous oxide emissions from irrigated cropping systems. *Soil Sci. Soc. Am. J.* **2010**, *74*, 436–445.
22. EPA. *Inventory of US greenhouse gas emissions and sinks: 1990-2001*; Environmental Protection Agency, Office of Atmospheric Programs: Washington, DC, 2003.
23. EPA. *Inventory of US greenhouse gas emissions and sinks: 1990-2002*; Environmental Protection Agency, Office of Atmospheric Programs: Washington, DC, 2004.
24. Mammarella, I.; Werle, P.; Pihlatie, M.; Eugster, W.; Haapanala, S.; Kiese, R.; Markkanen, T. M.; Rannik, U.; Vesala, T. A case study of eddy covariance flux of N_2O measured within forest ecosystems: quality control and flux error analysis. *Biogeosciences* **2010**, *7*, 427–440.
25. Del Grosso, S. J.; Wirth, T.; Ogle, S. M.; Parton, W. J. Estimating agricultural nitrous oxide emissions. *Eos* **2008**, *89*, 529–530.
26. Gentry, L. E.; David, M. B.; Below, F. E.; Royer, T. V.; McIsaac, G. F. Nitrogen mass balance of a tile-drained agricultural watershed in East-Central Illinois. *J. Environ. Qual.* **2009**, *38*, 1841–1847.
27. NASS. *Statistics by Subject*; National Agricultural Statistic Service, U.S. Department of Agriculture, 2010, http://www.nass.usda.gov/Statistics_by_Subject/index.php.
28. Snyder, C. S. *Fertilizer nitrogen BMPs to limit losses that contribute to global warming*. International Plant Nutrition Institute: Norcross, GA, 2008.http://www.eseap.org/ipniweb/portal.nsf/0/6d54abc2c92d9afa852549b0074ff59/$FILE/IPNI_Snyder_BMP-LR.pdf.
29. Staver, K. W.; Brinsfield, R. B. Using cereal grain winter cover crops to reduce groundwater nitrate contamination in the mid-Atlantic coastal plain. *J. Soil Water Conserv.* **1998**, *53*, 230–340.

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch001

Chapter 2

Nitrogen Source Effects on Nitrous Oxide Emissions from Irrigated Cropping Systems in Colorado

A. D. Halvorson* **and S. J. Del Grosso**

USDA, Agricultural Research Service, 2150 Centre Ave, Bldg. D, Ste. 100,
Fort Collins, CO 80526
***E-mail: ardell.halvorson@ars.usda.gov**

Nitrogen (N) fertilization is essential in most irrigated cropping systems to optimize crop yields and economic returns. Application of inorganic N fertilizers to these cropping systems generally results in increased nitrous oxide (N_2O-N) emissions. Nitrous oxide emissions resulting from the application of commercially available enhanced-efficiency N fertilizers [ESN, Duration III, SuperU, and UAN with AgrotainPlus] were compared with emissions from commonly used urea and urea-ammonium nitrate (UAN) fertilizers under differing tillage (conventional-till and no-till) practices and crop rotations (continuous corn, corn-barley, corn-bean). Significant differences in the amount of N_2O-N emitted among N sources were found. Some of the enhanced-efficiency N fertilizers reduced N_2O-N emissions as much as 50% when compared to dry granular urea and 35% compared to liquid UAN fertilizers commonly used by farmers in this semi-arid region. Further work is required to quantify the effectiveness of enhanced-efficiency N fertilizers in reducing N_2O-N emissions in other irrigated and non-irrigated systems, on different soil types, and in wetter climates.

Managing Nitrogen in Cropping Systems

Nitrogen fertilization to optimize crop yields and economic returns from agricultural production systems is an essential basic management decision (*2–4*) in

Not subject to U.S. Copyright. Published 2011 by American Chemical Society
In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

the U.S. Central Great Plains. The application of inorganic N fertilizer generally results in an increase in N_2O-N emissions (*5–7*), although increased emissions also occur with the application of organic sources (*8*, *9*). Nitrous oxide is a potent greenhouse gas that contributes to climate change, since the global warming potential of N_2O is ~296 times greater than CO_2, the reference greenhouse gas. In the U.S., agriculture contributes about 67% of the N_2O-N emissions (*10*), therefore, development of management practices to reduce N_2O-N emissions from cropping systems is very important.

Despite the essential role of agriculture and the development of enhanced-efficiency N fertilizers that can potentially decrease N_2O-N losses from N fertilizer application, there is relatively little known about the effects of agricultural management on N_2O-N emissions. An extensive literature review of greenhouse gas emissions from cropping systems by Snyder et al. (*7*) revealed that little information is available on N_2O-N emissions from cropping systems where direct comparisons have been made among different fertilizer N sources. They reported few studies evaluating the effects of commercially available controlled-release and stabilized N fertilizers on N_2O-N emissions. Based on data available, they reported that enhanced-efficiency N fertilizers (e.g. controlled-release, nitrification inhibitors, and urease inhibitors) might be management options to reduce N losses and thereby reduce indirect emissions of N_2O-N.

Recent research has shown that N fertilizer source can influence N_2O-N emissions from cropping systems. Venterea et al. (*11*) observed greater N_2O-N emissions from the application of anhydrous ammonia applied to corn in Minnesota than from urea-ammonium nitrate (UAN) and dry granular urea. They found no differences in N_2O-N emissions between conventional till (CT) and no-till (NT) corn systems when UAN was applied, but significant differences between CT and NT when urea was surface broadcast, with NT having the higher level of emissions. Venterea et al. (*12*) also reported higher N_2O-N emissions from anhydrous ammonia than from urea in another corn cropping system in Minnesota. Hyatt et al. (*13*) reported that a preplant application of polymer-coated urea fertilizers to potatoes grown on a loamy sand soil in Minnesota had yields equal to that from urea applied in multiple applications (5 to 6 times) during the potato growing season, with lower N_2O-N emissions from the polymer-coated urea sources compared to normal dry granular urea. Greenhouse gas (GHG) emissions resulting from fossil fuel consumption by an applicator tractor during the 5 to 6 applications of urea fertilizer would add to the total GHG emissions compared to the single preplant application of polymer-coated urea fertilizers.

Although polymer-coated N fertilizers have potential to decrease N_2O-N emissions in relatively short-time periods (20-40 days) after application, their longer-term effects on growing season N_2O-N emissions are relatively unknown. Halvorson et al. (*6*) observed that the application of polymer-coated urea in split applications with UAN or urea resulted in no immediate increase in N_2O-N emissions following application of the polymer-coated urea (May), but increased N_2O-N emissions later in the growing season (late June-August). The initial suppression of N_2O-N emissions following application of the polymer-coated urea was in contrast to increased emissions within days of UAN or urea application.

To determine the effectiveness of commercially available controlled-release and stabilized N fertilizers to reduce N_2O-N emissions under typical agricultural management practices in the semi-arid Central Great Plains, Halvorson et al. (*14*) initiated research to compare N_2O-N emissions from the application of urea and the polymer-coated urea, ESN, to CT and NT irrigated continuous corn production systems on a Fort Collins clay loam soil. They also compared the application of dry granular urea and a stabilized urea (SuperU, containing urease and nitrification inhibitors) in NT, irrigated corn-barley and corn-dry bean rotations on the same soil type. Halvorson et al. (*15*) also compared N_2O-N emissions from several inorganic N fertilizer sources (urea, UAN, SuperU, ESN, Duration III, and UAN+AgrotainPlus (*1*)) under NT, irrigated continuous corn production. The purpose of this chapter is to summarize and discuss the key results from the Halvorson et al. (*14*, *15*) studies.

Methodology

Fertilizer Sources Evaluated

The dry granular urea (46% N) and UAN (32% N) are commercially available N fertilizers commonly used by farmers in the central Great Plains of Colorado. The enhanced-efficiency N fertilizer sources evaluated were ESN (44%N), Duration III (43% N), SuperU (46% N), and UAN+AgrotainPlus (32% N). The polymer-coated urea fertilizers (ESN and Duration III) are registered products of Agrium Advanced Technologies, Sylacauga, AL. SuperU and AgrotainPlus contain a urease inhibitor [N-(n-butyl)-thiophosphoric triamide (NBPT)] and a nitrification inhibitor [dicyandiamide (DCD)]. SuperU and AgrotainPlus are registered products of Agrotain International, LLC, St. Louis, MO.

All N sources were surface banded near (0-10 cm) the corn row at crop emergence in mid-May in all studies, except for the NT barley crop where the fertilizers were broadcast applied at crop emergence, followed within 1 to 2 days with the application of 13+ mm of irrigation water. The N rates compared were 0 and 246 kg N ha^{-1} for corn, 0 and 156 kg N ha^{-1} for barley, and 0 and 56 kg N ha^{-1} for dry bean (*14*). The exception was for the 2008 N source study under NT continuous corn when 202 kg N ha^{-1} was applied to the corn (*15*).

Cropping and Tillage Systems

The conventional plow tillage (CT), continuous corn (CT-CC) cropping system used an intensive tillage system with disking and moldboard plow tillage after corn harvest in the fall followed by two roller harrow and land leveling operations in the spring followed by light cultivation if necessary to reduce soil erosion by wind. The no-till (NT) continuous corn (NT-CC) system was a plant, spray, and harvest system with no tillage operations. The other cropping systems used were a NT corn-barley rotation and a NT corn-dry bean rotation. Details of the tillage and crop production systems, as well as other field and laboratory procedures used to measure greenhouse gas (GHG) emissions are presented by Halvorson et al. (*4–6*, *14*, *15*). A linear-move, sprinkler irrigation system was used to apply water to the crops. A randomized complete block design with three replications was used with two GHG measurements per replication (total of 6 GHG measurements per treatment) for each sampling date. Nitrous oxide measurements were made 1 to 3 times per week, immediately following crop planting until crop harvest (growing season). A static, vented chamber technique was used to collect the gas samples in the field. A gas chromatograph was used to determine N_2O-N concentration in each gas sample [see (*5*, *14*, *15*) for more details on sampling protocol and methods].

Nitrous Oxide Emissions in Cropping System Studies

Continuous Corn

The N_2O-N fluxes resulting from urea and ESN application to the CT-CC and NT-CC systems are shown in Figure 1 for 2008. Following N fertilizer application, a rapid rise in N_2O-N fluxes occurred within several days after urea application in both tillage systems, with a small rise in N_2O-N flux following ESN application, then a decline to near background levels, followed by a rise again in N_2O-N flux from the ESN application from late-June through August in both tillage systems. The N_2O fluxes from the NT-CC system were much lower (50%) than from the CT-CC system both years. The delayed N_2c_2O-N emissions with the ESN source points out the need to maintain an intensive or frequent GHG sampling schedule for the entire growing season when evaluating polymer-coated or slow-release N products. Failure to do so could result in an erroneous characterization of N_2O-N emissions from such products.

The cumulative N_2O-N fluxes in 2007 for the CT-CC and NT-CC systems are illustrated in Figure 2, which clearly shows the rapid rise in N_2O-N emissions following urea application in both tillage systems, with a slower release following ESN application. The check treatment (no N applied for 8 yr) had the lowest level of N_2O-N emissions in both tillage systems. In both 2007 and 2008, N_2O-N emissions from the CT system were greater than from the NT system (Figure 3) with no significant difference in total N_2O-N emissions between urea and ESN in the CT system, but a significant reduction in N_2O-N emissions with ESN compared to urea in the NT system. The lower N_2O-N emissions in the NT system compared to the CT system were consistent with the observations reported by Halvorson et al. (*6*) who compared the effects of N rate (UAN) on N_2O-N emissions in the CT-CC and NT-CC systems from 2005-2006.

Corn-Barley and Corn-Bean

The application of a stabilized urea (SuperU) in the NT corn-barley (NT-CB) and NT corn-dry bean (NT-CDb) cropping systems in 2007 and 2008 resulted in significantly reduced growing season N_2O-N fluxes compared to dry granular urea. As was observed in the CT and NT continuous corn systems, there was a rapid rise in N_2O-N flux (data not shown) within days of urea and SuperU application to both of the NT-CDb and NT-CB rotations; however, the rise was much smaller for SuperU which possibly shows the benefit of the urease and nitrification inhibitors present in the SuperU fertilizer (*14*). The N_2O-N fluxes remained high for the first 20 days with urea, then declined to near background levels by about 40 days after application. The check with no N applied for 8 yr had the lowest level of N_2O-N emissions in both NT cropping systems. Total growing season N_2O-N emissions for these two NT cropping systems are shown in Figures 4 and 5. SuperU reduced N_2O-N emissions significantly compared to urea both years in both cropping systems.

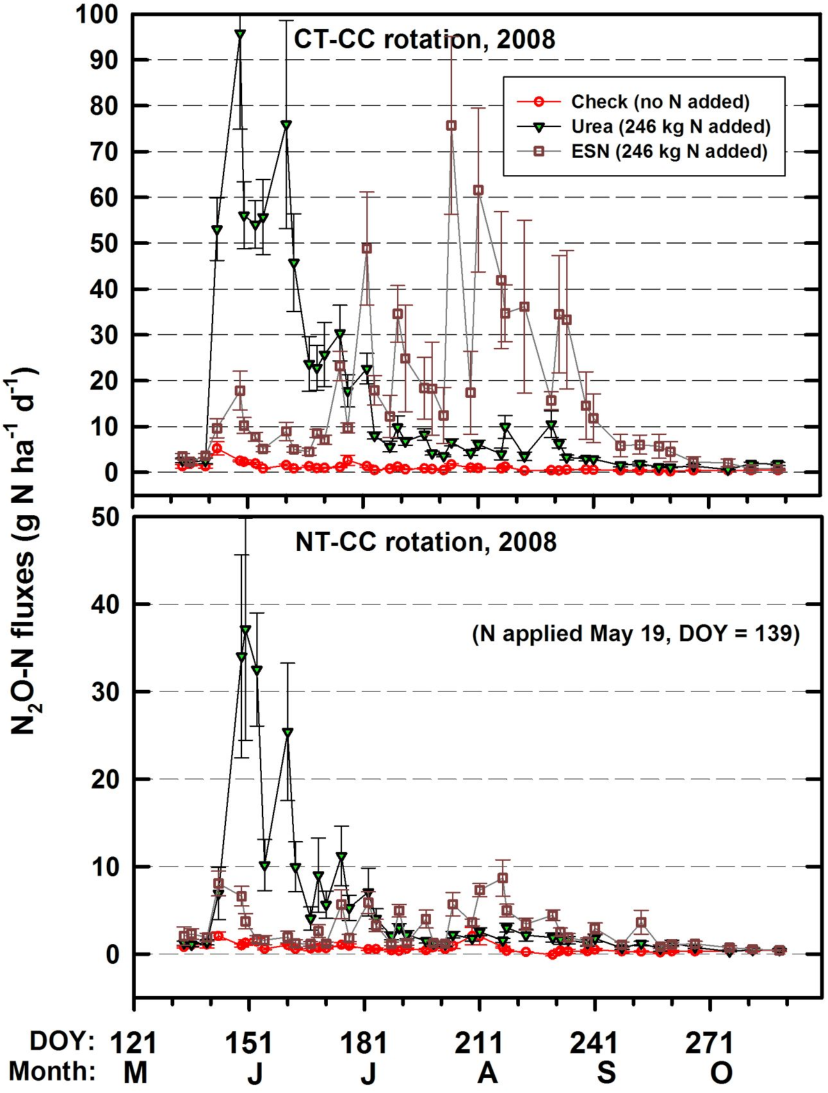


Figure 1. Daily N_2O-N fluxes with standard error bars in the CT-CC and NT-CC systems in 2008. Reproduced from reference (14).

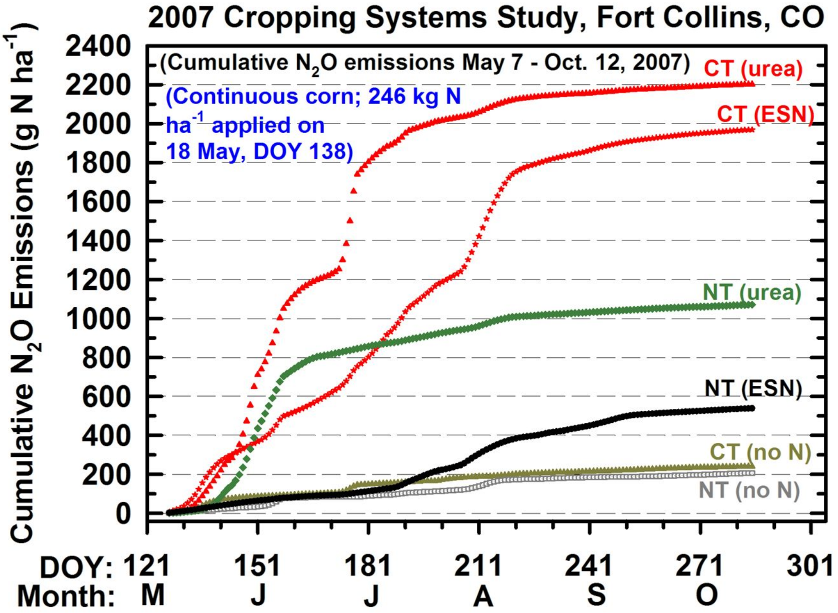


Figure 2. Cumulative daily N_2O-N emissions for each N source during the 2007 growing season in the CT-CC and NT-CC cropping systems.

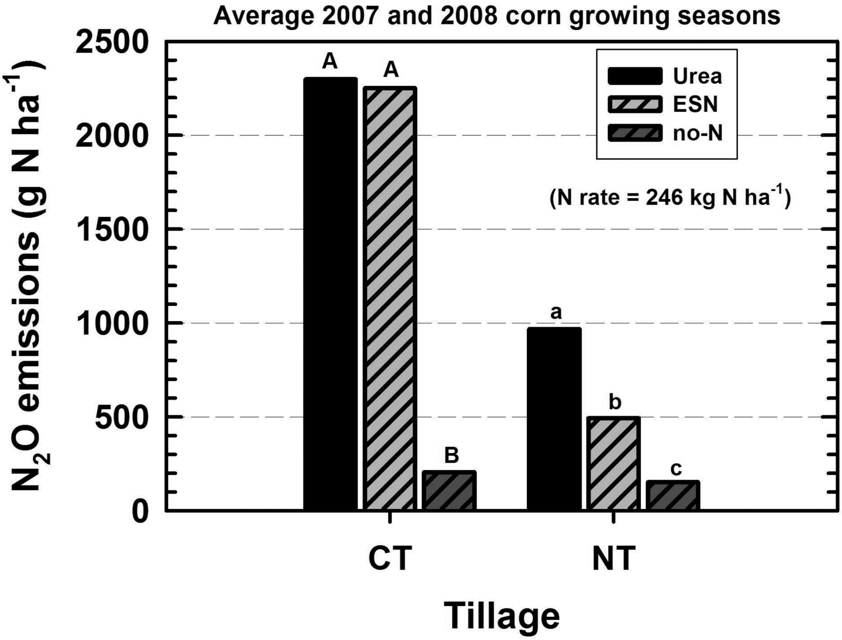


Figure 3. Average cumulative N_2O-N emissions for the 2007 and 2008 growing seasons for each N treatment in the CT-CC and NT-CC cropping systems. Reproduced from reference (14).

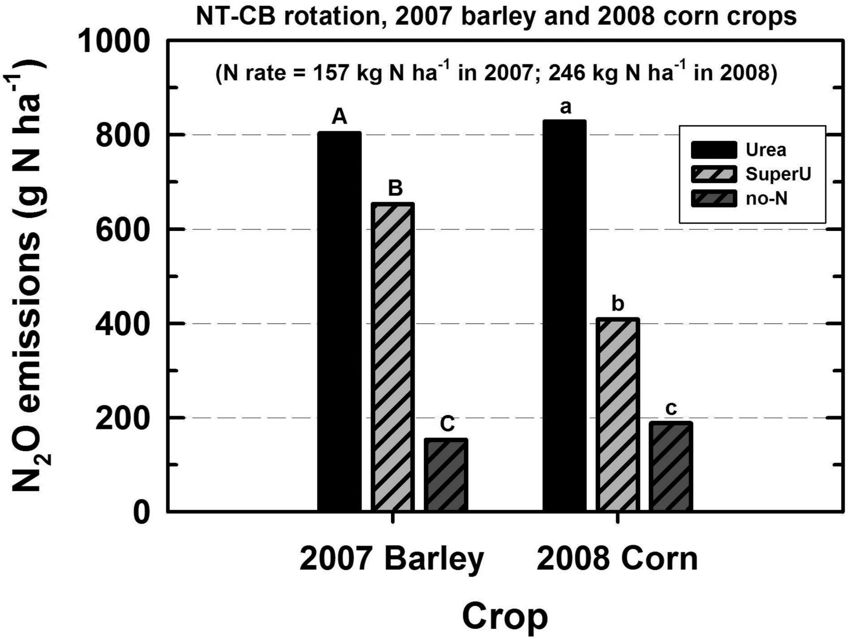


Figure 4. Cumulative N_2O-N emissions for the control, urea, and SuperU treatments during the 2007 (barley) and 2008 (corn) growing seasons in the NT-CB cropping system. Reproduced from reference (14).

Despite substantially different N application rates between barley and corn (157 and 246 kg N ha^{-1} applied, respectively) N_2O-N emissions in 2007 during the barley growing season with urea were nearly the same as the N_2O-N emissions during the corn growing season in 2008 (Figure 4). The growing season emissions from SuperU in 2007 were greater than in 2008. These results point out that cropping system, soil temperature and water content, and years have a significant effect on N_2O-N emissions, as reported by Mosier et al. (*5*).

In 2007 during the dry bean phase of the NT-CDb rotation which was fertilized with 56 kg N ha^{-1}, the dry bean crop was damaged by a residual herbicide. Therefore, corn was replanted in the field in early July as a silage crop with no additional N applied. The growing season N_2O-N emissions in 2007 were smaller than in 2008 with 246 kg N ha^{-1} applied (Figure 5) as would be expected due to the lower fertilizer N rate in 2007 (*6*).

In the NT cropping systems, we found decreased N_2O-N emissions from the application of a polymer-coated urea, ESN, and a stabilized urea, SuperU. The magnitude of reduction varied with NT cropping system and N rate applied. A significant reduction in N_2O-N emissions with the application of ESN in the CT continuous corn system compared to urea was not observed.

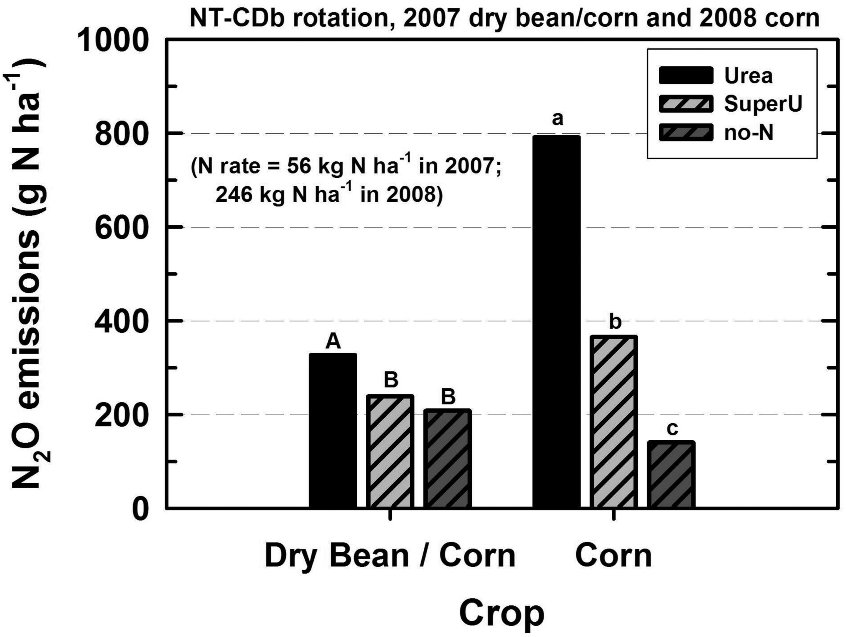


Figure 5. Cumulative N_2O-N emissions for the control, urea, and SuperU treatments during the 2007 (dry bean/corn) and 2008 (corn) phases of the NT-CDb cropping system. Reproduced from reference (14).

N Source Study

In 2007 and 2008, another study (*15*) was conducted to compare the effects of six different fertilizer N sources on N_2O-N emissions in an irrigated, NT continuous corn system. The fertilizers included urea, two polymer-coated ureas (ESN and Duration III), a stabilized urea (SuperU), UAN, and a stabilized UAN (UAN+AgrotainPlus). Following N fertilizer application in 2007 and 2008, cumulative N_2O-N fluxes from urea and UAN increased within days of application as shown for 2008 in Figure 6. Super U and UAN+AgrotainPlus had smaller immediate increases in N_2O-N fluxes following N application, with N_2O-N emissions returning to near background levels in about 40 days (see (*15*)). The ESN and Duration III treatments showed very little increase in N_2O-N emissions immediately after N application, but increases in N_2O-N fluxes occurred in late June through August, mainly following irrigation and precipitation events. As stated previously, this is an important observation for those evaluating the impact of polymer-coated N fertilizers or other controlled release N fertilizers on N_2O-N emissions. The frequency of GHG measurements need to be maintained at several times per week during the mid- to late-growing season to properly characterize the N_2O-N fluxes from controlled release or slow-release N fertilizers, possibly including manures. The check treatment (no N applied) had the lowest total growing season N_2O-N emissions.

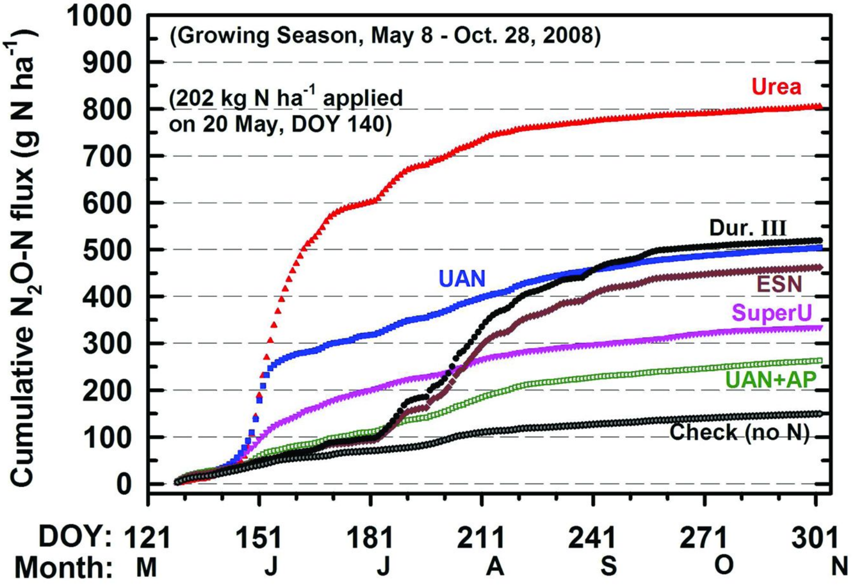


Figure 6. Cumulative daily N_2O-N emissions during the 2008 growing season for each N source in a NT-CC system. Reproduced from reference (15).

The two year average growing season N_2O-N emission for each N source evaluated is shown in Figure 7. Compared to urea, all other N sources had lower N_2O-N emissions for the growing season, with no differences among UAN, Duration III, and ESN. SuperU and UAN+AgortainPlus had lower emissions than the other N sources, but significantly greater than the check treatment. Averaged over the two years, the UAN treatment had a lower corn grain yield (11.87 Mg ha^{-1}) than urea (12.75 Mg ha^{-1}), but greater than the check treatment (8.92 Mg ha^{-1}) (*15*).

The loss of N_2O-N per unit of N applied for each N source is shown in Figure 8 for each year. The years are shown separately since a higher fertilizer N rate was used in 2007 than in 2008. The trends were similar both years with all sources showing a lower level of N_2O-N emissions per unit of N applied in 2008, except for urea which had a higher level of N_2O-N emissions in 2008 than in 2007. In general, urea had the highest level of N_2O-N emissions per unit of N applied both years, with UAN, ESN, and Duration III having lower emissions than urea, and Super U and UAN+AgrotainPlus having the lowest level of emissions. All N_2O-N emission levels were considerably lower than the default 1% from Tier I methodology of IPCC (*16*) used to estimate yearly N_2O-N emissions resulting from N fertilizer application. The degree of N_2O-N loss may vary strongly depending on cropping system, tillage management, and site-specific conditions as pointed out by Halvorson et al. (*14*). This indicates the need for source and site specific N_2O-N emission data before sound crop management decisions or mitigation policies can be formulated for effectively reducing N_2O-N emissions in a cropping region or area.

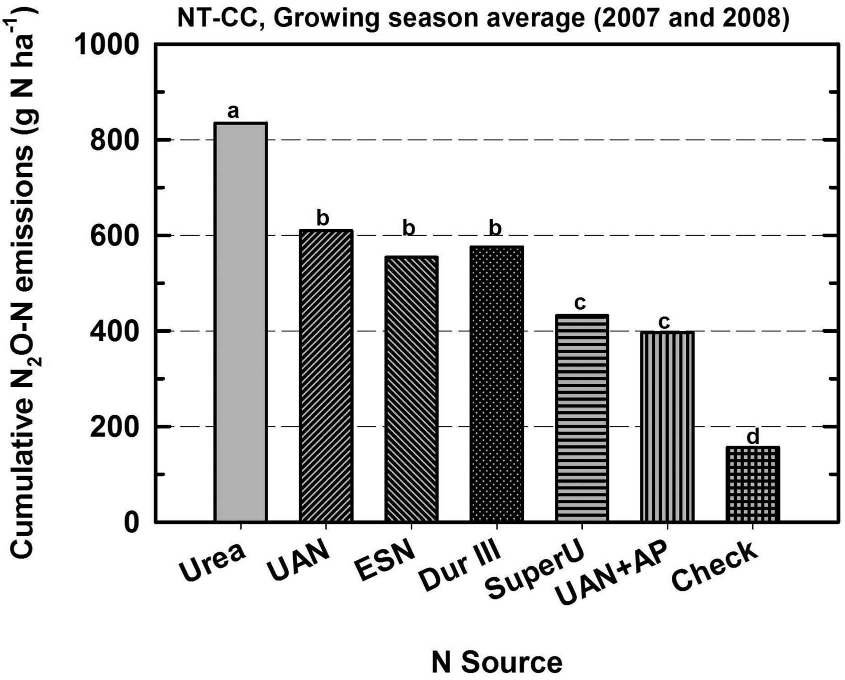


Figure 7. Two-year average total cumulative growing season N_2O-N emissions for each N source and check treatment in a NT-CC system. Developed from reference (15).

The effectiveness of N sources in reducing N_2O-N emissions in the NT-CC system compared to urea were in the order: UAN (27%), Duration III (31%), ESN (34%), SuperU (48%), and UAN+AgrotainPlus (53%). Compared to UAN, Duration III (6%) and ESN (9%) reduced N_2O-N emissions only slightly (not significant), but SuperU (29%) and UAN+AgrotainPlus (35%) reduced N_2O-N emissions significantly. The lower N_2O-N emissions of UAN compared to urea probably resulted because 33% of UAN is in the NO_3-N form and N_2O-N emissions from this NT-CC cropping system primarily resulted from the nitrification process and not denitrification. These data show that the enhanced-efficiency fertilizers offer potential for reducing N_2O-N emissions under irrigation in a semi-arid climate. The enhanced-efficiency N products need to be tested under other climatic conditions, soil types, and cropping systems to further evaluate their value in reducing N_2O-N emissions across the U.S.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

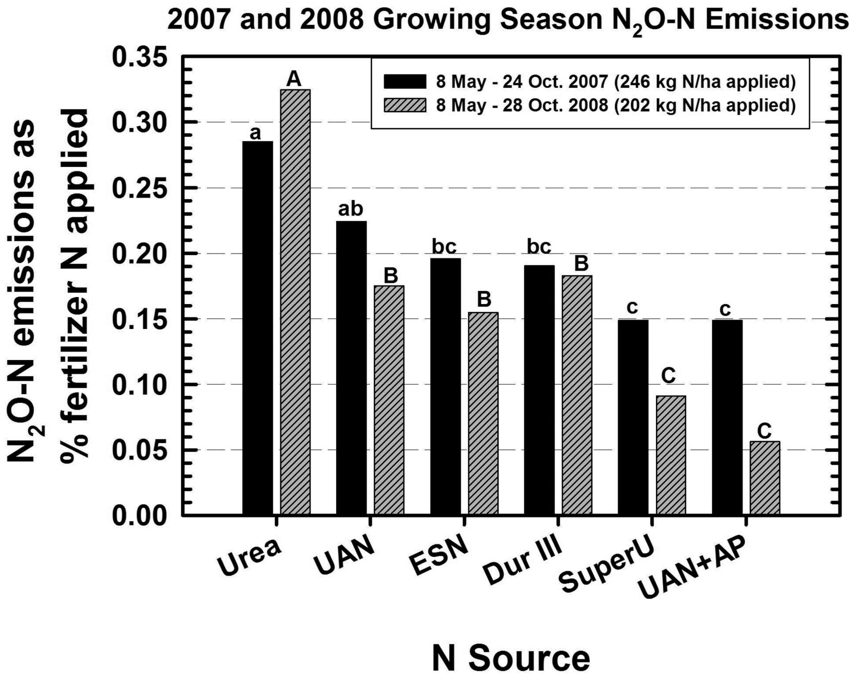


Figure 8. The N_2O-N loss per unit of N fertilizer applied during the 2007 and 2008 growing seasons, with each year shown separately due to different N rates in a NT-CC system. Developed from reference (15).

Expressing N_2O-N emissions as a function of grain yield is one way to account for variability in N_2O-N emissions and grain yield for each N source. Nitrogen fertilization is essential in most production systems to optimize grain yields and economic returns. The relationship between N_2O-N emissions and grain yields, averaged over 2 yr, is shown in Figure 9 for each N source evaluated in this study. Urea had the highest level of N_2O-N emissions per unit of corn grain yield, followed by lower emissions from UAN, Duration III, ESN, and SuperU; SuperU had N_2O-N emission levels no different than those from UAN+AgrotainPlus, which had the lowest emissions among the N sources, and the check had the lowest level of emissions per unit of yield. Despite low N_2O-N emissions, the check did not have sustainable grain yields (*2*, *17*). These studies show that the enhanced efficiency fertilizers have potential to reduce N_2O-N emissions per unit of grain production in this semiarid, irrigated corn production area of the Central Great Plains.

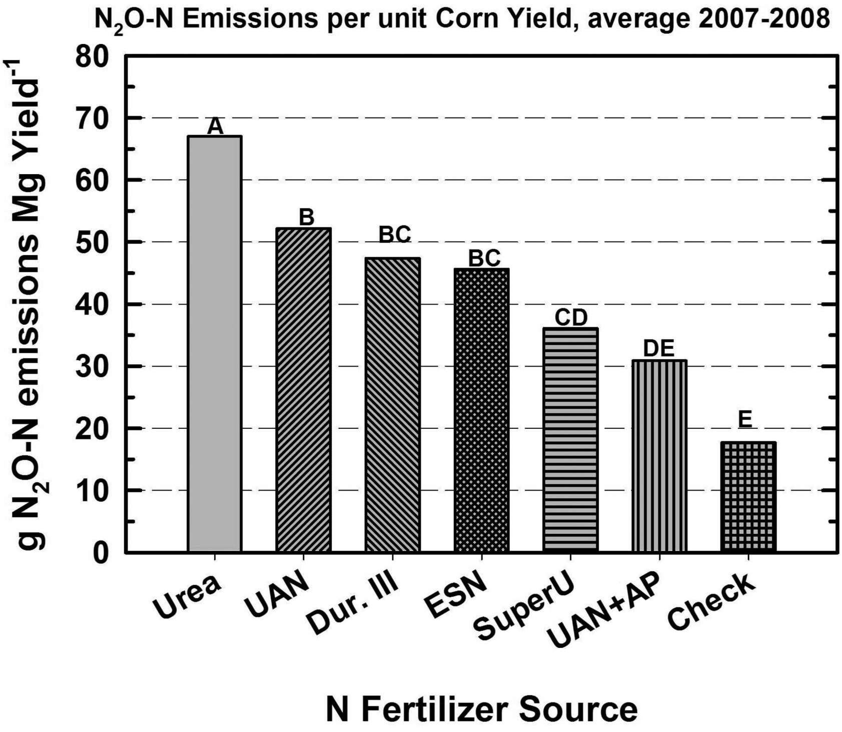


Figure 9. Two-year average growing season N_2O-N emissions per unit of grain yield for each N source in a NT-CC system. Developed from reference (15).

Summary

Nitrogen fertilization is essential in most irrigated cropping systems to optimize crop yields and economic returns. Application of inorganic N fertilizers to these cropping systems generally results in increased N_2O-N emissions. This chapter summarizes work (*14*, *15*) conducted by USDA-ARS near Fort Collins, Colorado on the effects of inorganic N fertilizer sources on N_2O-N emissions from irrigated cropping systems. The research shows that there are significant differences in the amount of N_2O-N emitted among N sources, and that emission measurements including controlled-release or slow-release N sources should span the entire growing season with sampling more than once per week. Commercially available enhanced-efficiency N fertilizers reduced N_2O-N emissions as much as 50% when compared to dry granular urea and 35% when compared to liquid UAN; fertilizers commonly used by farmers in this semi-arid region. Grain yields were not greatly affected by N source. Therefore, significant reductions in N_2O-N emissions per unit of grain production were observed in this study with the use of enhanced-efficiency N fertilizers. Further work is required to quantify the effectiveness of enhanced-efficiency N fertilizers in reducing N_2O-N emissions in other non-irrigated and irrigated systems, wetter climates, different soil types, and cropping systems.

References

1. Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the product by the authors or the USDA-ARS.
2. Archer, D. W.; Halvorson, A. D.; Reule, C. A. *Agron. J.* **2008**, *100*, 1166–1172.
3. Maddux, L. D.; Halvorson, A. D. In *Fertilizing for Irrigated Corn: Guide to Best Management Practices*; Stewart, W. M, Gordon, W. B., Eds.; International Plant Nutrition Institute: Norcross, GA, 2008; pp 3-1−3-6.
4. Halvorson, A. D.; Mosier, A. R.; Reule, C. A.; Bausch, W. C. *Agron. J.* **2006**, *98*, 63–71.
5. Mosier, A. R.; Halvorson, A. D.; Reule, C. A.; Liu, X. J. *J. Environ. Qual.* **2006**, *35*, 1584–1598.
6. Halvorson, A. D.; Del Grosso, S. J.; Reule, C. A. *J. Environ. Qual.* **2008**, *37*, 1337–1344.
7. Snyder, C. S.; Bruulsema, T. W.; Jensen, T. L.; Fixen, P. E. *Agric. Ecosyst. Environ.* **2009**, *133*, 247–266.
8. Mkhabela, M. S.; Gordon, R.; Burton, D.; Madani, A.; Hart, W. *Can. J. Soil Sci.* **2008**, *88*, 145–151.
9. Rochette, P.; Angers, D. A.; Chantigny, M. H.; Gagnon, B.; Bertrand, N. *Can. J. Soil Sci.* **2008**, *88*, 175–187.
10. USEPA. *Inventory of U.S. greenhouse gas emissions and sinks: 1990-2008.* U.S. Environmental Protection Agency, 1200 Pennsylvania Ave., N.W. Washington, DC 20460, 2010.
11. Venterea, R. T.; Burger, M.; Spokas, K. A. *J. Environ. Qual.* **2005**, *34*, 1467–1477.
12. Venterea, R. T.; Dolan, M. S.; Ochsner, T. E. *Soil Sci. Soc. Am. J.* **2010**, *74*, 407–418.
13. Hyatt, C. R.; Venterea, R. T.; Rosen, C. J.; McNearney, M.; Wilson, M. L.; Dolan, M. S. *Soil Sci. Soc. Am. J.* **2010**, *74*, 419–428.
14. Halvorson, A. D.; Del Grosso, S. J.; Alluvione, F. *Soil Sci. Soc. Am. J.* **2010**, *74* (2), 436–445.
15. Halvorson, A. D.; Del Grosso, S. J.; Alluvione, F. *J. Environ. Qual.* **2010**, *39*, 1554–1562.
16. IPCC. *IPCC guidelines for national greenhouse gas inventories - Volume 4: Agriculture, forestry and other land use.* URL: http://www.ipcc-nggip.iges.or.jp/public/2006gl/vol4.htm 2006, pp 11.1−11.54.
17. Archer, D. W.; Halvorson, A. D. *Soil Sci. Soc. Am. J.* **2010**, *74*, 446–452.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

Chapter 3

Nitrous Oxide Emissions at the Surface of Agricultural Soils in the Red River Valley of the North, U.S.A.

Rebecca L. Phillips* **and Cari D. Ficken**

USDA Agricultural Research Service, 1701 10th Ave. SW,
Mandan, ND 58554
***E-mail: rebecca.phillips@ars.usda.gov**

Agricultural fertilization worldwide reportedly contributes 6.2 Tg N_2O-N yr^{-1} to a total global source strength of 17.7 Tg N_2O-N yr^{-1}, and it is not entirely clear how fertilizer management influences the net flux of N_2O from soils. Data are lacking in agriculturally productive areas of the upper Midwestern United States, where sub-zero soil temperatures persist over a prolonged winter. Nitrous oxide emissions may be minimized by applying fertilizer N at variable, instead of single rates within crop fields. Using on-farm case studies in the Red River Valley of the North, U.S.A., variable-rate application of fertilizer N to crops was compared to single-rate. Varying the rate of N applied did not influence N_2O emissions, and greater amounts of N did not increase crop yields during this 2-year study. Background N_2O data measured at undisturbed grass sites suggest N_2O emissions at the surface of soils under production agriculture episodically, but not consistently, exceed background emissions.

Nitrous Oxide Production in Soil

Nitrous oxide (N_2O) gas is biogenically produced in soil by organisms as they use organic and inorganic forms of nitrogen (N) for energy and respiration. Several guilds of organisms utilize solid, dissolved, and gaseous forms of soil N, and a common by-product of these catabolic reactions is N_2O (*1*). There are two main pathways through which N_2O may be produced in soil. Reduced forms

Not subject to U.S. Copyright. Published 2011 by American Chemical Society
In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

of soil N, such as ammonia, may be used for energy, and the process results in the transformation of N into more oxidized forms of N, such as nitrate. This process is referred to as nitrification, and some N_2O gas is released during this transformation. In addition, nitrous oxide is produced during denitrification when soil oxygen is limited and nitrate, rather than oxygen, is used as an electron acceptor (*2*). Additional more specific pathways relevant to N_2O sources and sinks have been reported (*3*), but these are outside the scope of this chapter. Nitrification and denitrification broadly encompass major oxidative and reductive processes through which N_2O is produced in soil as a by-product. Both processes commonly occur simultaneously within the soil matrix and contribute to the net N_2O emissions measured at the soil surface.

Biologically-available N is required for microbial production of N_2O in soil. Soil N may become available as a result of organic matter decomposition, atmospheric N deposition, or the addition of N as fertilizer. Typically, reduced forms of N are nitrified to nitrate by chemotrophic organisms, and N_2O is released as a by-product. Heterotrophic nitrification, where soil organic carbon is used as an energy source, also occurs when oxygen is available (*4*). When oxygen is limiting, however, the nitrate produced during nitrification may be used by facultative aerobes in the process of denitrification, which also releases N_2O. Denitrification is a heterotrophic process, so a lack of soil carbon can limit denitrification rates (*5*). Emissions measured at the soil surface represent the amount of N_2O that has been produced by both oxidative and reductive processes, and has subsequently diffused from the soil pore spaces to the atmosphere aboveground. Physical changes that alter soil diffusivity, soil pore space volume, and soil pressure gradients will affect the transport of N_2O to the soil surface and then to the atmosphere (*6*).

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

Measurements of N_2O Emissions at the Soil Surface

While N_2O is biogenically produced belowground, researchers commonly study the net surface flux for a given area per unit time. Typically, measurements of N_2O involve collecting multiple samples of air within an enclosed chamber of a specific volume. Soil gas emanating from the surface accumulates in the chamber's headspace, and the molar change over time is used to calculate the rate of emission. This is referred to as the static chamber technique (*7*). The chamber is constructed over a bare soil footprint and the air is enclosed for a short (~30 minute) period of time, after which samples are collected with a syringe and the chamber top is removed. The samples are analyzed in a laboratory, where the concentration is determined using an electron capture detector following elution of the sample through columns in a gas chromatograph. The gas chromatograph is calibrated with known standards, so the amount of N_2O in the sample can be calculated by integrating the area under the chromatogram peak of intereSt. Usually, several static chamber sample sites are selected at random within plots to determine the spatial variability for soil N_2O. Emissions are also measured at several points in time to determine how they change with time, temperature, moisture, season, etc. A number of problems associated with this method have been reviewed in the literature (*8*), such as changes in chamber pressure that would affect the volume calculated within the enclosed headspace. However, most of the current knowledge of N_2O in agricultural soils is based on the static chamber technique. Due to the relatively simple protocol and wide availability of comparable data, this is likely to remain the most commonly published method for estimating N_2O emissions at the soil surface until more advanced measurement technologies become available.

Since surface N_2O emissions often represent the net amount produced by both oxidative and reductive processes, microbial production of N_2O is strongly regulated by soil oxygen status. Oxygen status belowground is heterogeneous and changes rapidly in soil, so a single measurement during the day may not adequately represent the rate of N_2O released over a 24-hr period. To determine diurnal variability, continuous measurements of N_2O in the field would be necessary, such as can be collected with tunable diodes, quantum cascade lasers or Fourier transform infrared spectroscopy (FTIR). As these technologies become available for field studies, researchers will gain a much greater understanding of how N_2O emissions change at the soil surface in response to management and soil conditions.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

N_2O Emissions and Agriculture

Food production comprises the single largest land use worldwide (*9*), and roughly two-thirds of N_2O emissions come from soils (*9*). Knowledge of how agricultural management influences sources and sinks of N_2O relative to crop yields is important to understanding potential anthropogenic impacts on climate forcing (*10*). One of the key factors influencing N_2O production is the fertilization of arable soils (*11–14*). Nitrogen can be oxidized by organisms capable of using reduced forms of N (such as ammonium) for energy, while oxidized forms (such as nitrate) can serve as terminal electron acceptors in the absence of oxygen. While the fertilizer N pathway within plants is well known, less known are interactions between soil biota and plants as they compete for fertilizer N.

While a number of studies indicate that N fertilization enhances microbial production of N_2O (*11–14*), laboratory and small-plot studies may not represent conditions typical of production agriculture fields. For example any disturbance to the soil (such as soil excavation and sieving) will affect N_2O emissions (*8*). Nitrous oxide is produced within soil micro-aggregates (*15*) throughout a soil pedon (*16*), so emissions data collected after removing soil from the field may not represent emissions in situ. Small-plot studies aim to simulate field conditions and minimize disturbance, but it is difficult to accurately scale-up small-plot studies to large, dryland production agriculture operations. For one, rates of fertilization used in experimental studies do not necessarily reflect agronomic rates used for crop production (*14*, *17*), and furthermore experimental plots often use irrigation (*10*, *18*). Additionally, heavy equipment usage on large farming operations would influence soil biological activity, yet heavy equipment is rarely used on experimental plots. Lastly, production agriculture operates under economic and climatic pressures that affect how soils and crops are managed. These conditions are also difficult to simulate. Any of these factors potentially alter soil gases, yet current knowledge of agricultural N_2O emissions is largely based on laboratory and small-plot studies. The question of how dryland production agriculture influences soil emissions of N_2O is difficult to fully address using soils that are disturbed, irrigated or fertilized at anomalously high rates. This chapter demonstrates factors potentially affecting surface N_2O emissions from fields managed for food production in the Red River Valley of the North (RRV), U.S.A.. The aim was to quantify and compare surface fluxes for large fields fertilized using either a) variable rate or b) single rate at two locations in the RRV using repeated measurements collected over 2 years.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

Two on-farm studies were initiated in an effort to quantify N_2O emissions for soils under dryland agriculture in the RRV (Figure 1). This region lies between North Dakota and Minnesota and extends from Canada to South Dakota. The RRV watershed lies on what was the southern tip of Lake Agassiz during the last glaciation, and soils here are considered some of the most fertile in the world. The growing season is short (May-August), and soils remain below freezing from November to March. The region typically receives over 50 cm of precipitation as rainfall each year. Monthly daily average temperatures during the growing season range from 10 to 25 °C. The highest air temperatures typically occur in July, with the first frost in September. Soils are usually cool and wet in April, so seeding is often delayed until May.

On-farm studies were initiated with independent growers in the RRV with the understanding that profitability would continue to be a priority. Growers understand their soils and crops to a greater extent than outside scientists and would likely make better management decisions. Researchers would not interfere with farming management decisions, and therefore the study would approximate conditions representative of production agriculture. This partnership required fundamental trade-offs: the advantage of performing research *in situ* would be accompanied by a lack of control over crop management decisions.

Current literature suggests that, by reducing total N inputs, variable-rate N fertilization alters the rate of N_2O emitted from the soil surface (*10*, *19–21*). Variable-rate involves the utilization of equipment that adjusts the amount of N applied according to management recommendations at specific geo-locations. Application rate is programmed according to maps loaded into a GPS that is attached to the applicator. These maps are commonly referred to as zoning maps because fields are broken down into several "zones", where specific rates are mapped as colors (Figure 2). As the applicator moves through fields from one zone to another, the application rate is automatically adjusted. Zoning maps are usually updated each year, depending on crop selection, soil tests, grower knowledge, and yields reported the previous year. The rate of N_2O emission is commonly referred to as flux, with units of N emitted as N_2O (mg N_2O-N m^{-2} d^{-1}). If the rate of fertilizer N application influences N_2O flux and the application of fertilizer at variable rates reduce total N inputs, then variable-rate application should result in lower emissions of N_2O than from application at a single rate.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

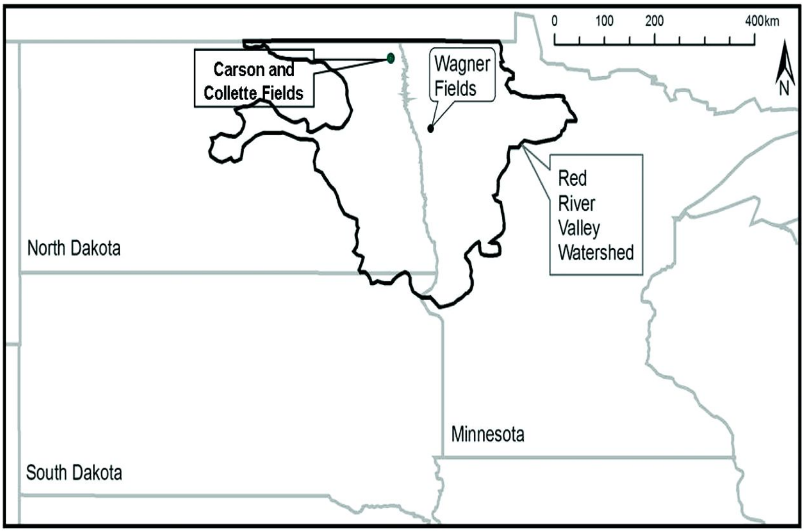


Figure 1. Map of the Red River Valley of the North watershed, U.S.A. and locations of experimental fields.

This assumption was tested by scientists at the University of North Dakota in cooperation with growers at farms in St. Thomas, ND and in Crookston, MN. Nitrogen was applied at variable rates for some fields and at a single, uniform rate for other fields. Each grower needed to fertilize at rates necessary to achieve yield goals for their soils according to personal knowledge and agronomist recommendations. Gas samples were scheduled for collection approximately 21 days following urea fertilization and 14 days after seeding. This delay was required because growers needed to complete all field activities before setting up stations for measurements at the soil surface. The goal was to compare relative differences in fluxes between variable and single rate fields rather than test for effects of fertilizer on N_2O emissions.

To avoid collecting data relevant only to a specific site or soil, research partnerships were initiated with growers at both north and central sections of the RRV, U.S.A.. Farthest to the north near the Canadian border, plots were selected at the Carson and Collette Farms near St. Thomas, ND. Near the center of the RRV between Fargo, ND and the Canadian border, plots were selected at A.W.G. Farms near Crookston, MN. All farms were operated for the purpose of generating profit through food production. Consequently, a) growers made crop management decisions and performed farm operations, b) large fields (15-65 ha) and full-scale farm equipment were employed, and c) large research plots were delineated and sampled repeatedly at several points. Thus, a) researchers could not dictate how crops were seeded, fertilized, harvested, or managed, b) researchers needed to collect data around farming activities, and c) vehicle access was limited at certain times to minimize traffic damage. This approach would yield realistic data for N_2O fluxes at a field scale under the constraints and pressures of production agriculture.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

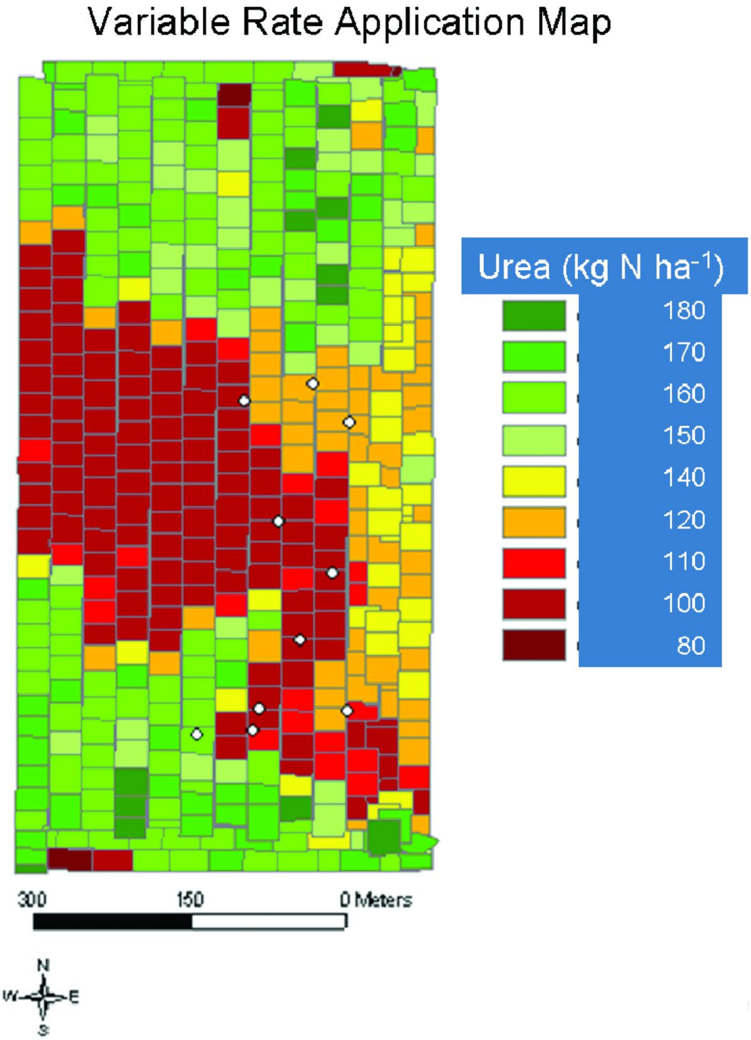


Figure 2. Example of a zoning map, where N fertilizer applied is presecribed for each geo-located zone. Actual amount deposited is recorded and displayed by color. In this example, the amount of urea applied to a St. Thomas crop field is represented by color. (see color insert)

On-Farm Investigation, St. Thomas, ND

This study was designed to determine if N_2O flux and crop yield varies with N fertilization management strategy for croplands located in St. Thomas, ND. Fields were selected both where fertilizer N as granular urea was applied annually using variable-rate application technology and where fertilizer N was applied at a single rate. Economics drive decisions in production agriculture, so rates of fertilizer N were determined by trusted local agronomists. Prescriptions were based on previous data collected by yield monitors on harvesting equipment and soil testing results. Where yields were higher than average, fertilizer N was prescribed at a higher rate. Where yields were lower than average, fertilizer was prescribed at a lower rate (Simplot, Inc., personal comm.).

Six fields (~20 ha each), located within a kilometer of each other, were selected for this study (Figure 3). Soils history and taxonomy were similar among all fields, which use spring wheat, potato, and sugarbeet rotation schedule. Soil texture was a clay loam, with a bulk density of 1.1 g cm^{-2} from 0- 15 cm. Soil pH was 8.0 with 2.5% organic carbon and 1.0% inorganic carbon. All six fields were seeded to hard red spring wheat in April 2003 and potatoes in May 2004. Each spring, three fields received fertilizer N applied at variable rates while the remaining three fields received a single rate of fertilizer N per field (Figure 3). An application monitor on the equipment determined actual rate applied each year, and these are the data reported here. One 8-ha plot was placed in each field at least 20 m from field edges. Within each plot, 10 points were randomly selected using 1-m aerial photography (Figure 3) and geo-located with a sub-meter, real-time differential Trimble Geo XT Global Positioning System (GPS) Beacon receiver (Trimble Navigation, Sunnyvale, CA, U.S.A.). At each of the 10 points within each plot, a permanent station was deployed, where gas flux measurements were repeatedly collected multiple times over two growing seasons using the static chamber method described previously. At each station and collection time, soil samples and soil temperature data were collected. On a single day, the first pair of plots was sampled (one plot from each treatment). The next day, the second pair was sampled, and the third pair was sampled on the third day. All sixty stations were sampled over an approximate 10-day time period. Field measurements were interrupted by rain, crop dusting, and harvest.

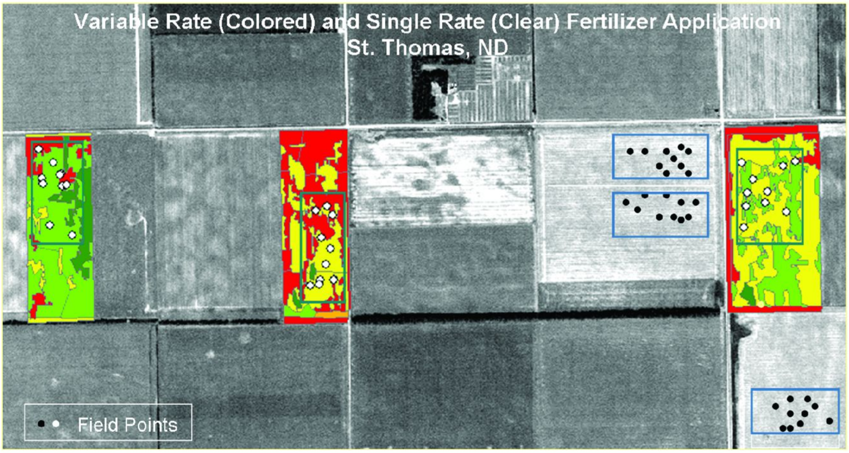

Variable Rate (Colored) and Single Rate (Clear) Fertilizer Application
St. Thomas, ND
• • Field Points

Figure 3. Experimental design for fields owned by P. Carson and A. Collette in St. Thomas, ND and 2003 zoning maps. The three colored fields represent variable amounts of urea prescribed by agronomists. Clear plots represent areas where a single rate of urea was applied. (see color insert)

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

The N fertilization rate at each station was determined each year, based on actual application maps (Figure 2). The random points generated within each plot included points which received high, medium and low concentrations of N. Since the zoning map and application rate changes annually, the plots were not stratified by management zone for N_2O flux measurements. The same points were repeatedly sampled over two years, yet the amount of N applied to each point changed each spring. Soil percent water-filled pore space (%WFPS) was determined for each station during gas flux sampling. Net fluxes of N_2O were expected to vary with %WFPS, soil temperature, and the amount of N applied. Differences in the total amount of N applied for both variable- and single-rated fields were calculated. Flux data were collected repeatedly at a point, and were analyzed to determine if fertilizer application technique (variable vs. single rate) affected N_2O flux under variable environmental conditions. Researchers aimed to determine if variable rate application technology resulted in (1) less fertilizer N applied, (2) lower emissions of N_2O at the soil surface, and (3) greater crop yields, as compared to fields where fertilizer was applied at a single rate. In 2004, yield measurements were stratified by management zone, so a balanced test for the effect of management zone on yield could be performed.

2003 Growing Season Results

The three fields fertilized at a single rate in 2003 (Figure 3) received a similar amount of N, on average, as fields fertilized using variable-rate technology. Average N applied to the variable-rate field was 160 kg N ha^{-1}, whereas average N applied to the single-rate field was 158 kg N ha^{-1}. Wheat yield and total aboveground dry matter production were also similar for both variable-rate and single-rate fields (Figure 4), with aboveground production ranging from 11,000 to 11,500 kg ha^{-1} (Figure 5). Nitrous oxide fluxes were also similar between treatments. Fluxes for variable-rate and single-rate fertilizer management ranged from 0 to 13 mg N_2O-N m^{-2} d^{-1} (Figure 6), and it is clear that N_2O flux did not necessarily increase with the rate of N application. In 2003, the highest values for N_2O flux (> 8 mg N_2O-N m^{-2} d^{-1}) were recorded at fertilization rates between 140 and 175 kg N ha^{-1}. For sites fertilized with less than 120 kg N ha^{-1} (represented by 34% of the total observations), N_2O fluxes were less than 4 mg N_2O-N m^{-2} d^{-1}. These data suggest that the addition of N beyond 120 kg ha^{-1} may have enhanced N_2O flux, but there were too few observations to be certain. Fluxes collected in 2003 were similar between those sites where N was applied at 180-190 kg N ha^{-1} and those where N was applied at 110 kg N ha^{-1} was applied. Peaks were episodic, and a predictable, linear relationship between fertilizer N application rate and N_2O flux was not found (Figure 6). However, N_2O flux was affected by soil %WFPS and soil temperature. When soils were both cool (<15 °C) and dry (<15 %WFPS), fluxes were consistently less than 2 mg N_2O-N m^{-2} d^{-1}. The rate of fertilizer N application in 2003 (ranging from 110 to 200 kg N ha^{-1}) did not statistically alter fluxes. These field points were measured again in 2004 following spring fertilization and potato seeding.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

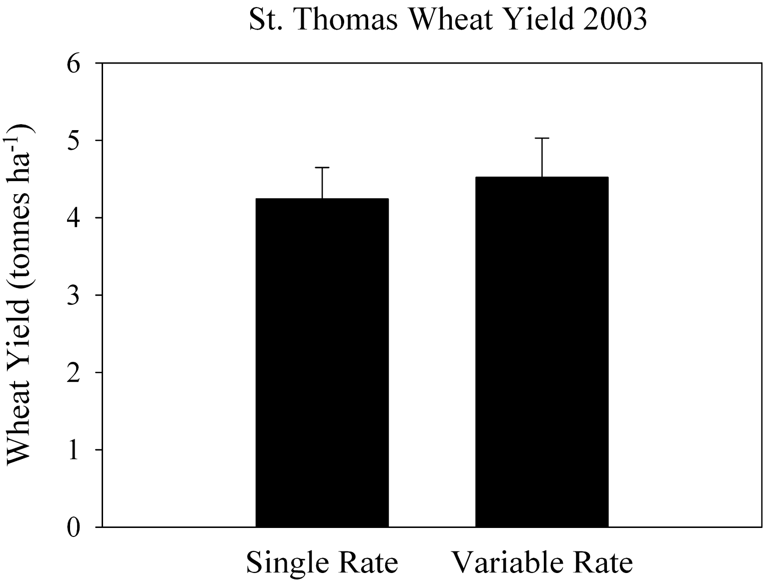


Figure 4. Average wheat yield data collected by yield monitors for variable rate versus single rate field management at St. Thomas, ND field sites.

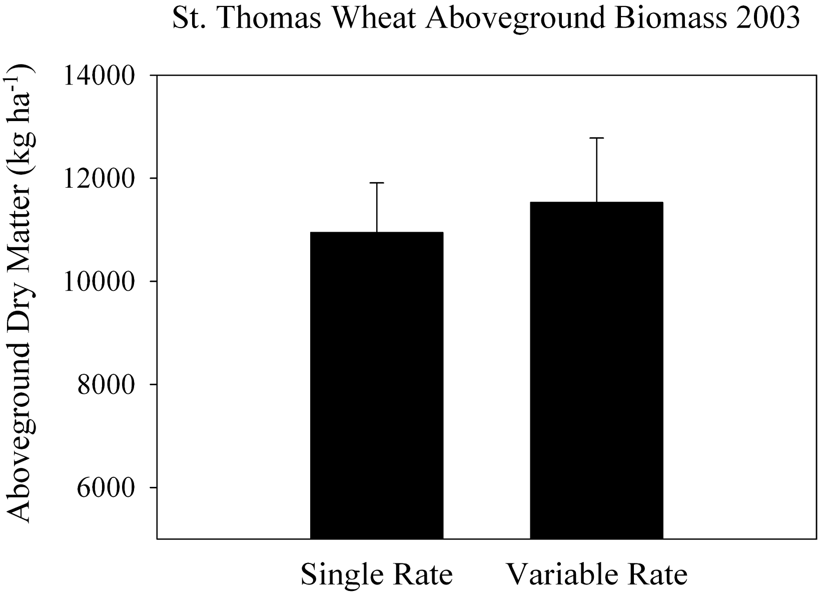


Figure 5. Average amount of dry matter produced in 2003 for variable rate versus single rate fields at St. Thomas, ND field sites. Aboveground biomass was harvested at random points using manual techniques.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

2004 Growing Season Results

The six fields seeded to wheat in 2003 (Figure 3) were seeded to potato in 2004, so zoning maps and fertilization recommendations were adjusted by growers. Fields fertilized at a single rate in 2004 received less total N, on average, than fields fertilized at a variable-rate. Variable-rate field-average N application in 2004 was 170 kg N ha^{-1}, whereas single-rate field-average N application was 90 kg N ha^{-1}. Application of more N did not result in a consistent increase in N_2O emissions (Figure 6). Similar to 2003, high flux values (4 of the 527 observations) were found in 2004 for stations fertilized at approximately 200 kg N ha^{-1} (Figure 6). In 2004, all fluxes at points fertilized at less than 100 kg N ha^{-1}, were less than 2 mg N_2O-N m^{-2} d^{-1}. In both 2003 and 2004, N_2O fluxes were more strongly affected by temperature and moisture than by fertilization rate.

Potato yield data were collected at three points within each management zone for all fields just prior to harvest in September 2004. Results indicated that the amount of N applied did not influence yield (Figure 7), and there was no difference in yield among management zones. In summary, the amount of N applied in 2003 and 2004 did not sufficiently explain variability in N_2O flux and did not have a significant effect on wheat or potato yield for these clay loam soils in St. Thomas, ND.

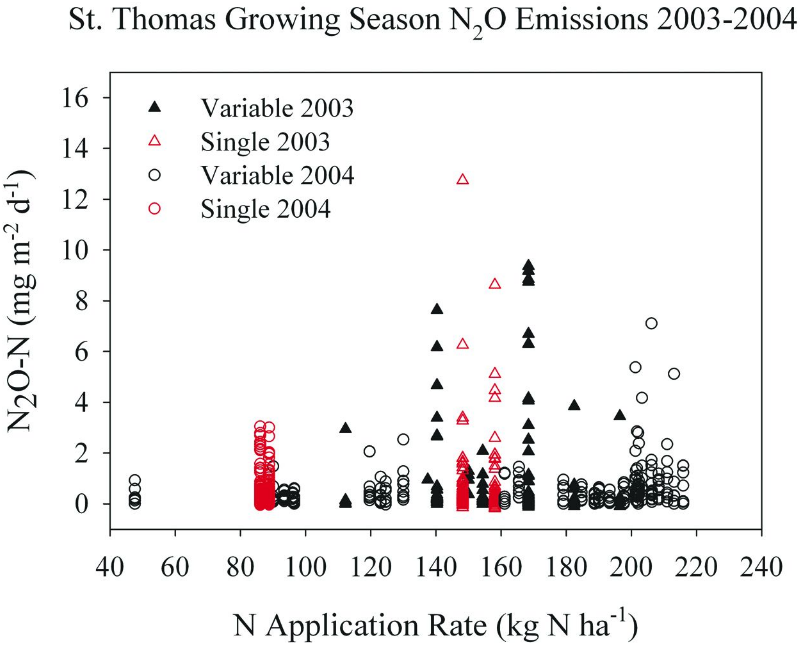


Figure 6. Nitrous oxide emissions data collected during the 2003 (symbolized by triangles) and 2004 (symbolized by circles) growing seasons plotted against fertilizer N application rate prescribed for each sample point at St. Thomas, ND field sites. (see color insert)

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

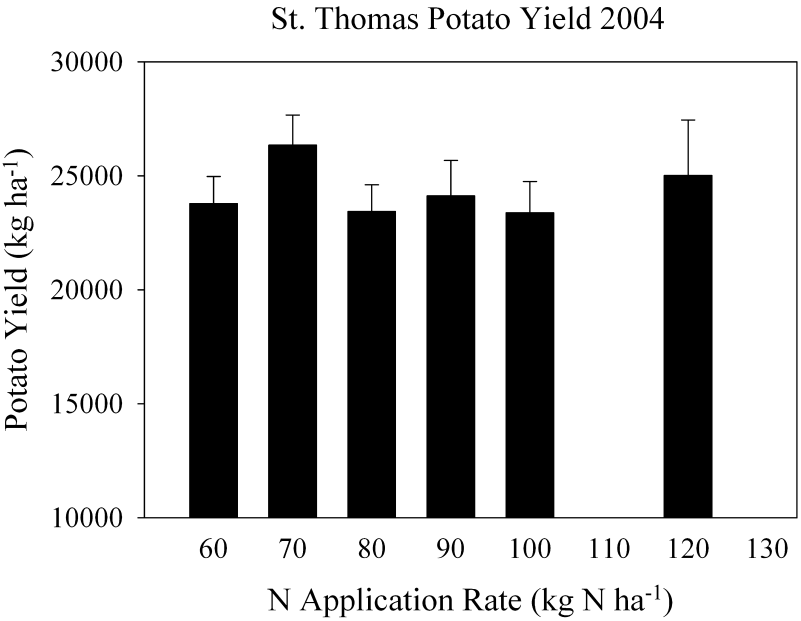


Figure 7. Average potato yield data collected using manual harvesting techniques plotted against the amount of fertilizer applied to a specific geo-location at St. Thomas, ND field sites.

On-Farm Investigation, Crookston, MN

Using croplands owned by A.W.G. Farms in Crookston, MN, a similar study was designed to determine if N_2O flux and yield vary with N fertilization management. For this study, a 65-ha variable-rate field and a 40-ha single-rate field were selected. Three 8-ha plots were delineated inside each field at least 20 m from field edges (Figure 8). In April 2004, the 65-ha field received fertilizer N using variable-rate technology, while the 40-ha field received fertilizer N at a single rate. Rates of fertilization were determined by the producer, based on personal knowledge and yield history (G. Wagner, personal comm.). Fields were then seeded to hard red spring wheat. The grower elected to fertilize again in autumn 2004, so soil N_2O emissions were collected again during the winter of 2005. During the winter, stations were cleared of snow to the top of the station, leaving 5 cm of snow cover at the soil surface. Nitrous oxide fluxes were collected at 10 random points within each plot using the static chamber method, in accordance with the St. Thomas work described above. One treatment pair was sampled on one date, followed by the second and the third pair. Between April and September 2004, a total of 540 N_2O station measurements were collected. Between January and April 2005, access to the stations was limited, so a total of 200 N_2O station measurements were collected.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

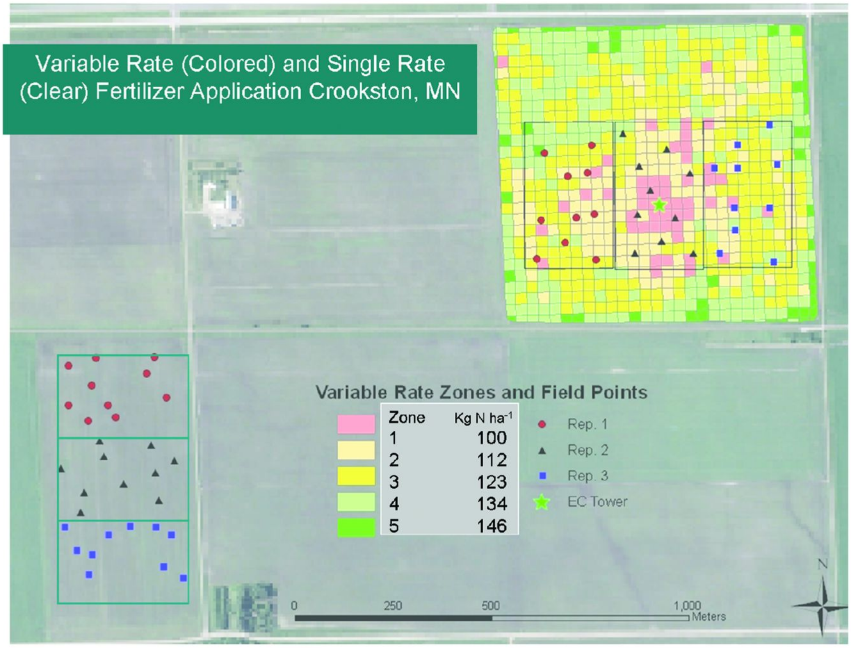

Variable Rate (Colored) and Single Rate (Clear) Fertilizer Application Crookston, MN
Variable Rate Zones and Field Points
Zone
Kg N ha-1
1 100
2 112
3 123
4 134
5 146
Rep. 1
Rep. 2
Rep. 3
EC Tower
0
250
500
1,000
Meters
N

Figure 8. Experimental design and 2004 zoning map for fields owned by A W. G. Farms at Crookston, MN. The colored field represents variable amounts of anhydrous ammonia prescribed by landowner Gary Wagner. Clear plots represent areas where a single rate of anhydrous ammonia was applied. (see color insert)

Land-use history and soil series (fine, silty, mixed, superactive frigid Aeric Calciaquoll) was similar for both variable- and single-rate fields (Figure 8), both with a history of wheat, sugarbeet and soybean rotations. Soil texture was classified as clay with a high water holding capacity (0.9 g water per g soil). Bulk density at the 0-15 cm depth increment was 1.3 g cm^{-2}. This contrasted with the St. Thomas soils, which were well-drained clay loam soils with a moderate water holding capacity (0.7 g water per g soil) and lower bulk density (1.1 g cm^{-2}). Soil pH was 7.9, which was similar to the pH of 8.0 at St. Thomas. Fields at Crookston were fertilized with anhydrous ammonia and gas sample collection began seven weeks after fertilization, whereas the fields at St. Thomas were fertilized with urea and gas sample collections began three weeks after fertilization. Differences in gas sample initiation were due to weather and field access limitations. Previous work indicates that N_2O fluxes at the soil surface are influenced by soil moisture and temperature, fertilizer form (*22*), fertilizer amount (*23*), fertilizer application timing (*24*), and soil texture (*25*). The effects of fertilization on greenhouse gas fluxes at the soil surface tend to peak within the first eight weeks after N application (*11–14*). Residual effects of fertilization could have affected emission data collected within the first few weeks of fertilization.

Soil percent water-filled pore space (%WFPS) was determined for each station during gas flux sampling, and soil temperature was measured each day. Net fluxes of N_2O were expected to vary with %WFPS, soil temperature, and the amount of fertilizer N most recently applied. Total N applied was calculated for both variable- and single-rated fields. Flux data were collected repeatedly at each point, and were analyzed to determine if fertilizer application technique (variable vs. single rate) affected N_2O flux under variable environmental conditions. As with the St. Thomas investigation, researchers aimed to determine if variable-rate application technology resulted in (1) less fertilizer N applied, (2) lower emissions of N_2O at the soil surface, and (3) greater crop yields, as compared to fields where fertilizer was applied at a single rate.

2004 Growing Season Results

Soils fertilized using variable-rate technology in 2004 received less total N, on average, than soils fertilized at a single rate. The average N applied to the variable-rate field was 123 kg N ha^{-1}, whereas the average N applied to the single-rate field was 132 kg N ha^{-1}. Wheat yields were similar among fields and did not increase with rate of fertilization (Figure 9). Nitrous oxide flux data are plotted in Figure 10 against the specific rate of N applied at each of the 60 points. Variable-rate technology application did not reduce emissions of N_2O to the atmosphere, and greater rates of N application did not predictably enhance emissions of N_2O (Figure 10). While higher N inputs sometimes resulted in greater emissions of N_2O, the pattern was not consistent. The highest N_2O emissions in 2004 were observed during one day in July, at two points fertilized at 110 and 120 kg N ha^{-1}, when soil temperature was 17 °C and %WFPS was 60%. Crookston N_2O fluxes, in general, were greater than those observed at St. Thomas. The capacity for soils to hold water at Crookston, where soils are clay, was greater than the capacity for soils to hold water at St. Thomas, where soils are clay loam. Average %WFPS for St. Thomas was 30%, while average %WFPS for Crookston was 60%. Soils with higher %WFPS are known to enhance soil microbial gas production (*26*).

2005 Winter Results

Rates of N applied to measurement stations in autumn 2004 included two points where the application rate was less than 100 kg N ha^{-1}. Gas samples were collected at points where application rates were 0, 30, 100, 105, 120, 130, and 138 kg N ha^{-1}. Average N input for the entire variable-rate field was 115 kg N ha^{-1}, while the average N input for the single-rate field was 130 kg N ha^{-1}. Fertilization rates in autumn were similar to those from the previous spring, and winter N_2O emissions were on the same scale as those from the growing season. The highest emissions occurred at the end of the winter sampling period, after the spring thaw in 2005 (Figure 10). The highest emission peak (16 mg N_2O-N m^{-2} d^{-1}) was observed during the April data collection, when soil temperature was 15 °C and %WFPS was 60%. High N_2O emissions at the soil surface are common after soils thaw (*27*), which may be due to high soil water content and the release of N_2O previously produced and trapped in ice (*28*). Peaks due to N inputs generally occur within the first 8 weeks following fertilization. In this case, the highest N_2O peak occurred over four months after the fall fertilization. It is likely that freezing

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

and thawing may interact with fertilizer N to affect N_2O flux (*29*), but more research in this area is needed. Moreover, without continuous measurements, it is not known how long these emission peaks are sustained. Advanced measurement technologies would enhance the science needed to understand the effects of agriculture on N_2O emissions at the soil surface.

Background N_2O Emissions

Background or reference N_2O emissions refer to fluxes measured from sites that are not fertilized, tilled or otherwise disturbed by agricultural production practices. Emissions from these sites can be used to indicate what level of N_2O emissions might be expected in the absence of agriculture. For the St. Thomas and Crookston investigations, one native prairie remnant at each location was sampled at each data collection time. Prairie remnants are rare, so multiple reference sites were not available for inclusion in the experimental design. These data are spatially limited, but multiple measurements over time can indicate how emissions change, so a background threshold can be identified. Nitrous oxide emissions occurred at the surface of these undisturbed soils and often ranged between 1 and 2 mg N_2O–N m^{-2} d^{-1}. Emissions greater than 2 mg N_2O–N m^{-2} d^{-1} were found only in four of the 55 prairie incubations. These background data are similar to reference data collected at semi-arid prairie sites, where emissions exceeded 2 mg N_2O–N m^{-2} d^{-1} in only three of the 705 incubations (*24*). When cropland emissions (Figures 6 and 10) are compared to background levels, these field data suggest that cropland soil N_2O emissions were greater than reference sites in some but not all cases.

If background N_2O emissions were 2 mg N_2O–N m^2 d^{-1}, then observations over 2 mg N_2O–N m^2 d^{-1} reported at the St. Thomas and Crookston sites are most likely associated with agricultural land use. These high emissions may result from current or historical agricultural soil disturbance, such as topsoil and native plant removal. Loss of soil will affect physicochemical properties, such as water holding capacity, cation-exchange capacity, and microbial communities. Further, the loss of native grassland plants will affect fungal hyphae, soil aggregation, soil aeration, and water infiltration. Nitrous oxide is initially produced within soil microsites, and then migrates to the soil surface through soil pore spaces; consequently, any of the factors associated directly or indirectly with agriculture could affect N_2O emitted at the surface.

We identified “background” flux based on remnant prairie data collected adjacent to crop fields as approximately 2 mg N_2O–N m^2 d^{-1}. Those observations greater than 2 mg N_2O–N m^2 d^{-1} were evaluated separately for the purpose of identifying how often fluxes at St. Thomas and Crookston exceeded background. We found 45 observations collected at St. Thomas exceeded 2 mg N_2O–N m^2 d^{-1}. These represented 6% of the 870 total data points collected from 2003 to 2004. We found 66 observations collected at Crookston exceeded 2 mg N_2O–N m^2 d^{-1}. These observations represented 9% of the 740 total data points collected from 2003 to 2005. The low number of high emissions may be attributed to limitations in large-scale “on-farm” experiments, where weather, logistics, and

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

farming practices (spraying, etc.) precluded regular data collection. The fact that less than 10% of the emissions data were above background for both Crookston and St. Thomas suggests that high N_2O emissions may not occur as frequently as expected. Inclusion of observations directly following fertilization would have increased the number of observation above background. This study did not aim to quantify emissions directly following fertilization, as these reports using small, randomized block designs are common in the literature. Instead, emissions are evaluated for fields managed by producers in the business of production agriculture.

The 45 observations above background collected at St. Thomas and the 66 observations above background collected at Crookston are graphed together with respect to fertilization rate in Figure 11. Highest emissions (from 9 to 16 mg N_2O–N m^2 d^{-1}) were recorded at fertilization rates ranging from 100-150 kg N ha^{-1}. Average emissions were approximately 6 mg N_2O–N m^2 d^{-1} for those points fertilized between 150 and 220 kg N ha-1. Average emissions were approximately 3 mg N_2O–N m^2 d^{-1} for those points fertilized at less than 100 kg N ha^{-1}. While it is clear from these data (Figure 11) that fertilization rate positively influences N_2O flux, the relationship was not linear. These data suggest lower emissions may be achieved when N is applied at rates less than 100 kg N ha^{-1}.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

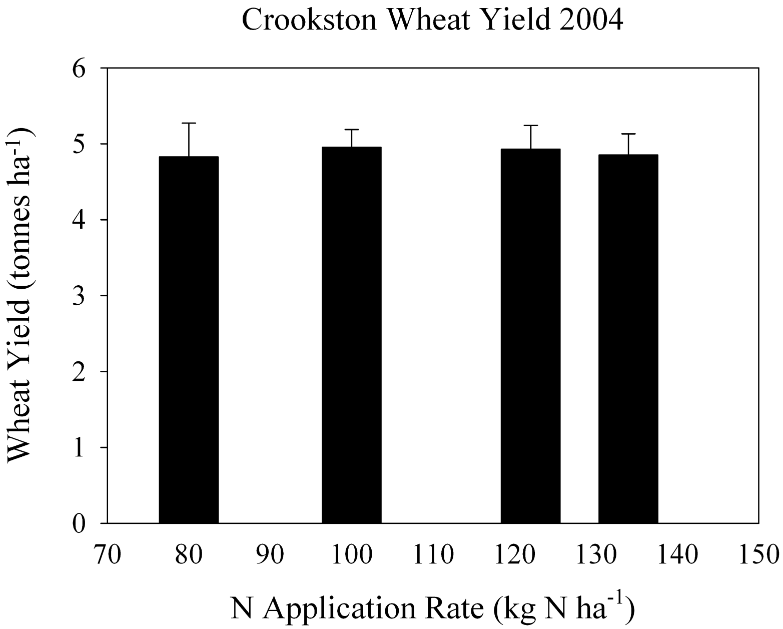


Figure 9. Average wheat yield data and fertilizer N application rate collected using applicator measurement systems and yield monitors for variable rate and single rate fields at Crookston, MN field sites.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

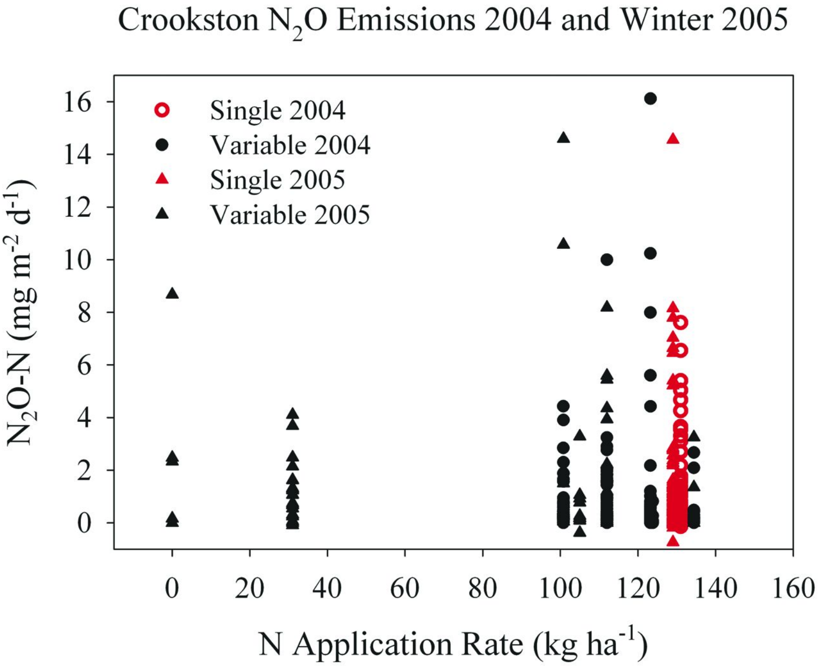


Figure 10. Nitrous oxide emissions data collected during the 2004 growing season (symbolized with circles) and winter 2005 (symbolized with triangles) plotted against fertilizer N application rate prescribed for each sample point at Crookston, MN field site. (see color insert)

For data that exceeded the 2 mg N_2O-N m^{-2} d^{-1} background level, the amount of N_2O-N emitted per unit of fertilizer N applied at that point was calculated to provide a rough comparison of the maximum N utilization rates at Crookston and St. Thomas. For each flux in Figure 11, there is a corresponding fertilization rate. We summed the Crookston fluxes and the Crookston fertilization rates for all 66 observations. The flux sum was divided by the fertilizer rate sum. This provided an indication of the proportion of N added that was emitted as N_2O-N. For Crookston, 6% of the fertilizer N applied was emitted as N_2O. Using St. Thomas data in a similar manner, 3% of the fertilizer N was emitted as N_2O. In this case, the average percentage of fertilizer N emitted as N_2O was twice as high for Crookston than for St. Thomas. This was found in spite of the time delay between fertilization and flux collection. It is clear from this example that emissions of N_2O at the soil surface and microbial response to N inputs vary with soil properties for agricultural fields located in a similar climate.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

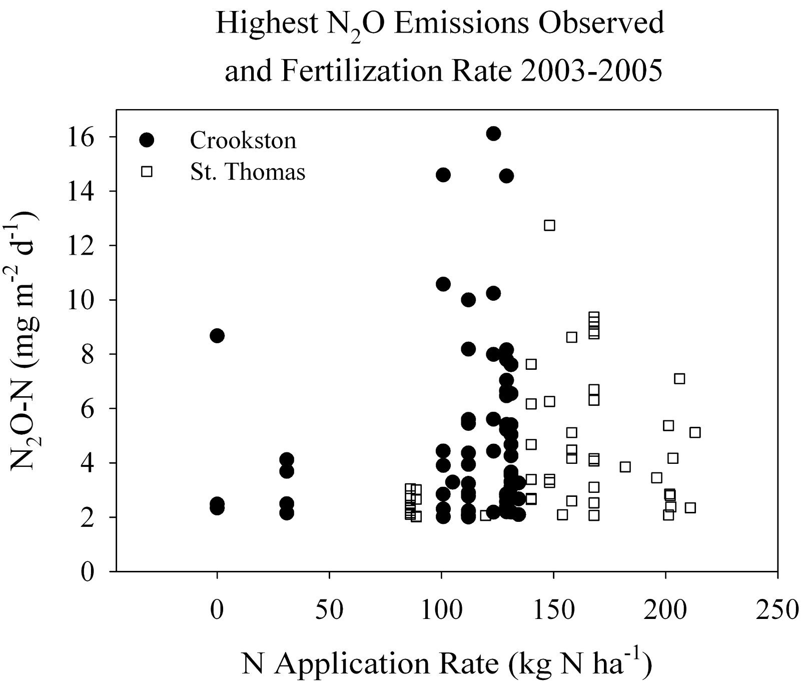


Figure 11. Nitrous oxide data for both St. Thomas, ND and Crookston, MN field sites that exceeded the background level of 2 mg N_2O-N m^{-2} d^{-1} versus fertilizer application rate.

Clay loam soils at St. Thomas were fertilized more heavily, yet net N_2O fluxes (for those observations that exceeded background and therefore could be attributed to agriculture), were 50% lower per unit of N added than for the less-fertilized clay soils at Crookston. Higher clay content in Crookston soils could explain some of the differences in N_2O fluxes between the research areas, if all other factors were equal. Clay content is a key input parameter to simulation models of N_2O[25], and interacts with rainfall to affect %WFPS, soil oxygen status, and water infiltration. Rainfall at both research areas were similar, yet the Crookston average %WFPS was twice as high as the average %WFPS at St. Thomas. Another factor that could contribute to observed differences between Crookston and St. Thomas is the form of fertilizer N application (*30*). Nitrous oxide emissions following application of anhydrous ammonium are reportedly higher than emissions following application of urea. Anhydrous ammonia, which is knifed into the ground, may also have had a more sustained effect of gas emissions. Soil water status and fertilizer form likely contributed to the unique responses to fertilizer inputs between Crookston and St. Thomas observations. Understanding effects of agriculture on N_2O emissions for fields in production require further study, for less than 10% of the on-farm agricultural soil emissions measured in these case studies exceeded background levels measured at native reference sites.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

Summary

While the addition of fertilizer N to agricultural soils may be intended to benefit the plant only, fertilizer addition also stimulates microbial production of greenhouse gases that are transported to the atmosphere. Greater amounts of fertilizer N, however, do not necessarily induce incrementally greater N_2O emissions or crop yield for soils in the northern Great Plains (*24*). For example, N_2O emissions measured at the surface of fertilized soils under dryland maize production were not consistently greater than uncultivated, native grassland soils (*24*). In the RRV case studies reported here, peaks in N_2O emissions occurred both at spring thaw and during the growing season when soil temperatures were greater than 15 °C. Contrary to results for plot studies where N inputs are high (*11–14*), agronomic rates of fertilizer N for large fields in production may not have a sustained effect on N_2O emitted at the soil surface. Application of fertilizer N at agronomic rates does not necessarily increase cumulative N_2O emissions for dryland agriculture, particularly at rates below 100 kg N ha^{-1} (*17*).

Variable-rate technology could result in a reduction of fertilizer N to agricultural fields, but this will depend upon producer goals. In cases where higher yields are desired (e.g. St. Thomas), agronomists will often prescribe higher N inputs. In cases where lower input costs are desired (e.g. Crookston), producers may decide to reduce N application rate. Here, there were some differences between agronomic rates applied by single versus variable-rate growers, but they were not followed by significant differences in N_2O emissions at the soil surface. Based on these agronomic data, microbial production of N_2O varies more with soil properties and environmental conditions than with management. However, the static chamber method for collecting N_2O data does not provide the information necessary to capture important episodic peaks of N_2O flux. It is possible that researchers here and in other studies “miss” the effect of fertilizer N on N_2O emissions due to these methodological constraints. Advancing knowledge of factors driving N_2O emissions measured at the soil surface requires measurement systems that capture spatiotemporal variability inherent to nitrification and denitrification processes in soils.

Nitrous oxide fluxes observed at the surface of soils at St. Thomas and Crookston were likely by-products of both soil nitrification and denitrification. Both processes require an N source, either as ammonium or nitrate, respectively. Therefore, N_2O fluxes were expected to vary with the rate of fertilizer N application for similar soils. Instead, fluxes varied with soil temperature and percent water-filled pore space. Soil characteristics, such as clay content, and the physical environment, such as temperature, may control microbial production of N_2O more strongly than the amount of fertilizer N. Denitrification tends to contribute more to spikes in N_2O flux data than nitrification (*2*). Oxygen has a greater difficulty diffusing through water than air, so anoxic conditions are expected at higher soil water contents. As soil oxygen declines at higher %WFPS values, the rate at which microorganisms denitrify increases (*26*). Nitrifying organisms also respond positively to soil water content with increased rates of nitrification when some soil oxygen is present (*2*). The average %WFPS for clay loam soils at St. Thomas was 30% and the average %WFPS for clay soils at

Crookston was 60%. Nitrous oxide fluxes at Crookston were greater than fluxes at St. Thomas (Figures 6 and 10). Anoxic microsites within the soil profile could have been sources of denitrification at either location (*16*), but denitrification was more likely at Crookston, where clay content and %WFPS were greater. Advance in N_2O management will likely require identification of the dominant microbial processes that contribute to N_2O fluxes *in situ*.

While crop yield was not the focus of this study, it is interesting that neither wheat and potato yields at St. Thomas, nor wheat yields at Crookston varied with the amount of N applied. In these dryland agriculture case studies, addition of more N did not result in greater yield. These observations suggest there may be room for reductions in rates of fertilizer N, which would potentially reduce costs for fertilizer and microbial production of greenhouse gases (*27*). Additional studies are needed to determine thresholds where the addition of more N would no longer affect yield but might instead stimulate microbial activity and increase trace gas emissions (*27*, *31*). The management of fertilizer N to minimize greenhouse gas emissions is feasible, but this will require a close examination of how N is utilized by both microbes and plants *in situ*, and also more advanced measurement techniques.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

References

1. Firestone, M. K.; Davidson, E. A. Microbial basis of NO and N_2O production and consumption in soil. In *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*; Andreae, M. O., Schimel, D. S., Eds.; John Wiley & Sons: New York, 1989; pp 7−21.
2. Maag, M.; Vinther, F. P. Nitrous oxide emission by nitrification and denitrification in different soil types and at different soil moisture contents and temperatures. *Appl. Soil Ecol.* **1996**, *4*, 5–14.
3. Kampschreur, M. J.; Poldermans, R.; Kleerebezem, R.; Van Der Star, W. R. L.; Haarhuis, R.; Abma, W. R.; Jetten, M. S. M.; Van Loosdrecht, M. C. M. Emission of nitrous oxide and nitric oxide from a full-scale single-stage nitritation-anammox reactor. *Water Sci. Technol.* **2009**, *60*, 3211–3217.
4. Inubushi, K.; Naganuma, H.; Kitahara, S. Contribution of denitrification and autotrophic and heterotrophic nitrification to nitrous oxide production in andosols. *Biol. Fertil. Soils* **1996**, *23*, 292–298.
5. Beauchamp, E. G.; Trevors, J. T.; Paul, J. W. Carbon sources for bacterial denitrification. *Adv. Soil Sci.* **1989**, *10*, 113–142.
6. Stepniewski, W.; Horn, R.; Martyniuk, S. Managing soil biophysical properties for environmental protection. *Agric., Ecosyst., Environ.* **2002**, *88*, 175–181.
7. Whalen, S. C.; Reeburgh, W. S. Interannual variations in tundra methane emissions: A 4-year time series at fixed sites. *Global Biogeochem. Cycles* **1992**, *6*, 139–159.
8. Davidson, E. A.; Savage, K.; Verchot, L. V.; Navarro, R. Minimizing artifacts and biases in chamber-based measurements of soil respiration. *Agric. For. Meteorol.* **2002**, *113*, 21–37.

9. Prather, M.; Ehhalt, D.; Dentener, F.; Derwent, J.; Dlugokencky, E.; Holland, E. A.; Isaksen, I.; Katima, J.; Kirchhoff, P.; Matson, P. A.; Midgley, P.; Wang, M., Atmospheric chemistry and greenhouse gases. In *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*; Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., van der Linden, P. J., Dai, X., Maskell, K., Johnson, C. A., Eds.; Cambridge University Press: Cambridge, UK, 2001; pp 240−287.
10. Mosier, A. R.; Halvorson, A. D.; Reule, C. A.; Liu, X. J. Net global warming potential and greenhouse gas intensity in irrigated cropping systems in northeastern Colorado. *J. Environ. Qual.* **2006**, *35*, 1584–1598.
11. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. Emissions of N_2O and NO from fertilized fields: Summary of available measurement data. *Global Biogeochem. Cycles* **2002**, *16*, 1058–1071.
12. Breitenbeck, G. A.; Bremmer, J. M. Effects of rate and depth of fertilizer application on emission of nitrous oxide from soil fertilized with anhydrous ammonia. *Biol. Fertil. Soils* **1986**, *2*, 201–204.
13. Chantigny, M. H.; Prévost, D.; Angers, D. A.; Simard, R. R.; Chalifour, F. P. Nitrous oxide production in soils cropped to corn with varying N fertilization. *Can. J. Soil Sci.* **1998**, *78*, 589–596.
14. Mosier, A. R.; Parton, W. J.; Valentine, D. W.; Ojima, D. S.; Schimel, D. S.; Delgado, J. A. CH_4 and N_2O fluxes in the Colorado shortgrass steppe:1. Impact of landscape and nitrogen addition. *Global Biogeochem. Cycles* **1996**, *10*, 387–399.
15. Sey, B. K.; Manceur, A. M.; Whalen, J. K.; Gregorich, E. G.; Rochette, P. Small-scale heterogeneity in carbon dioxide, nitrous oxide and methane production from aggregates of a cultivated sandy-loam soil. *Soil Biol. Biochem.* **2008**, *40*, 2468–2473.
16. Parkin, T. B. Soil microsites as a source of denitrification variability. *Soil Sci. Soc. Am. J.* **1987**, *51*, 1194–1199.
17. Phillips, R. L.; Podrebarac, F. Net fluxes of CO_2, but not N_2O or CH_4, are affected following agronomic-scale additions of urea to prairie and arable soils. *Soil Biol. Biochem.* **2009**, *41*, 2011–2013.
18. Halvorson, A. D.; Mosier, A. R.; Reule, C. A.; Bausch, W. C. Nitrogen and Tillage Effects on Irrigated Continuous Corn Yields. *Agron. J.* **2006**, *98*, 63–71.
19. Amos, B.; Arkebauer, T. J.; Doran, J. W. Soil surface fluxes of greenhouse gases in an irrigated maize-based agroecosystem. *Soil Sci. Soc. Am. J.* **2005**, *69*, 387–395.
20. Robertson, G. P.; Paul, E. A.; Harwood, R. R. Greenhouse gases in intensive agriculture: Contributions of individual gases to the radiative forcing of the atmosphere. *Science* **2000**, *289*, 1922–1925.
21. Sainju, U. M.; Jabro, J. D.; Stevens, W. B. Soil carbon dioxide emission and carbon content as affected by irrigation, tillage, cropping system, and nitrogen fertilization. *J. Environ. Qual.* **2008**, *37*, 98–106.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

22. Venterea, R. T.; Burger, M.; Spokas, K. A. Nitrogen oxide and methane emissions under varying tillage and fertilizer management. *J. Environ. Qual.* **2005**, *34*, 1467–1477.
23. Sehy, U.; Ruser, R.; Munch, J. C. Nitrous oxide fluxes from maize fields: relationship to yield, site-specific fertilization, and soil conditions. *Agric., Ecosyst., Environ.* **2003**, *99*, 97–111.
24. Phillips, R. L.; Tanaka, D. L.; Archer, D. W.; Hanson, J. D. Fertilizer application timing influences greenhouse gas fluxes over a growing season. *J. Environ. Qual.* **2009**, *38*, 1569–1579.
25. Del Grosso, S. J.; Parton, W. J.; Mosier, A. R.; Walsh, M. K.; Ojima, D. S.; Thornton, P. E. DAYCENT National-Scale Simulations of Nitrous Oxide Emissions from Cropped Soils in the United States. *J. Environ. Qual.* **2006**, *35*, 1451–1460.
26. Linn, D. M.; Doran, J. W. Effect of water-filled pore space on carbon dioxide and nitrous oxice production in tilled and on-tilled soils. *Soil Sci. Soc. Am. J.* **1984**, *48*, 1267–1272.
27. Gregorich, E. G.; Rochette, P.; VandenBygaart, A. J.; Angers, D. A. Greenhouse gas contributions of agricultural soils and potential mitigation practices in Eastern Canada. *Soil Tillage Res.* **2005**, *83*, 53–72.
28. Phillips, R. L. Denitrification at Sub-Zero Temperatures in Arable Soils: A Review. In *Sustainable Agriculture*; Springer: New York, 2009; Vol. 28, pp 87−93.
29. Phillips, R. L. Organic agriculture and nitrous oxide emissions at sub-zero soil temperatures. *J. Environ. Qual.* **2007**, *36*, 23–30.
30. Venterea, R. T.; Burger, M.; Spokas, K. A. Nitrogen Oxide and Methane Emissions under Varying Tillage and Fertilizer Management. *J. Environ. Qual.* **2005**, *34*, 1467–1477.
31. Guo, J.; Zhou, C. Greenhouse gas emissions and mitigation measures in Chinese agroecosystems. *Agric. For. Meteorol.* **2007**, *142*, 270–277.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch003

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

Chapter 4

Exchange Fluxes of NO_X, NH_3, and N_2O from Typical Wheat, Paddy, and Maize Fields in the Yangtze River Delta and North China Plain

Yuanyuan Zhang, Shuangxi Fang, Junfeng Liu, and Yujing Mu*

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, Beijing 100085, China
***E-mail: yjmu@rcees.ac.cn**

The exchange fluxes of NO_X, NH_3 and N_2O between two typical agricultural fields and the atmosphere were investigated in the Yangtze River Delta (YRD) and North China Plain (NCP). The average fluxes of NO and NH_3 from the wheat field in the YRD were 79 and -5.1 ng N m^{-2} s^{-1}, and from the paddy field were 3.7 and 34.8 ng N m^{-2} s^{-1}, respectively. The fertilize-induced emission factors (EFs) as NO-N and NH_3-N from the wheat field were 2.3% and 1%, and from the paddy field were 0.09% and 3.5%, respectively. Remarkable yearly variation of N_2O emissions from the investigated NCP maize field was observed, with average fluxes of 72.1 ng N m^{-2} s^{-1} in 2008 and 30 ng N m^{-2} s^{-1} in 2009 and with EFs of 3.78% in 2008 and 1.08% in 2009. The average NO and NH_3 fluxes from the maize field in 2009 were 36.5 ng N m^{-2} s^{-1} and 94.0 ng N m^{-2} s^{-1}, respectively. Based on the molar ratios of NO/N_2O, the emissions of NO_X and N_2O from the maize field were mainly ascribed to nitrification processes. Returning wheat straw back into the maize field could significantly reduce NO_X and NH_3 emissions.

Introduction

Agricultural fields have been recognized as an important source of atmospheric nitrous oxide (N_2O), nitrogen oxide (NO_X) and ammonia (NH_3) gas emission. These gases play an important role in regional and global environments (*1*). N_2O is involved in the depletion of stratospheric ozone (O_3) and consequently

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

the ozone layer (*2–4*). NO_X are major precursors of tropospheric oxidants and have important contributions to tropospheric O_3 and acid deposition (*5*). NH_3, the only alkaline gas in the atmosphere (*6*), regulates atmospheric acidity (*7*), contributes to atmospheric aerosols and adds to soil acidification (*8*).

The gaseous emission of N_2O, NO_X and NH_3 from agricultural fields are mainly from nitrogen fertilization (*1*, *9–13*). In the global budgets, estimated emission from agricultural soils ranged 0.11-6.3 Tg N yr^{-1} for N_2O (*14*, *15*) and 4-21 Tg N yr^{-1} for NO (*16–19*). NH_3 from agricultural fields was estimated to be ~23% of its global emission (*10*). The large uncertainty estimations are mainly due to the spatial-temporal variations of different plant, soil, and microbial environments. To reduce the uncertainties, more sampling sites and long term field measurements are needed.

The North China Plain (NCP) is one of the most important grain production regions in China. It accounts for 23% of Chinese cropland area while providing 39% of the total food in China (*20*). The Yangtze River Delta (YRD, Southeast of China) also accounts for a large proportion of total grain production in China. For example, the YRD produced 20% of total Chinese wheat harvest which accounted for 5% of the total Chinese grain production in 1990 (*21*). To meet increasing food demands, there has been a sharp increase in the use of nitrogen (N) fertilizers in China. Chinese fertilizer use accounts for more than a quarter of total N consumption in the world (*22*). According to Chinese statistical information (*23*), the current annual chemical fertilizer application rate (~866 kg ha^{-1} yr^{-1}) has increased more than three fold since 1980. In order to estimate the impact of agricultural activities on N cycling, it is essential to investigate the soil surface-atmospheric exchanges of N gases above different agricultural fields. Although some works on this topic have been completed in these regions of China (*24–29*), additional studies on the exchange of NO_X and NH_3 between agricultural fields in the YRD and NCP regions of China and the atmosphere are required to further the current understanding. Although most of the completed studies focused on N_2O emission (*20*, *29–38*), the large differences of fertilizer-induced N_2O-N emission factors (EFs, ranging from 0.006% to 1.94%) and average fluxes (ranging from 4.21 to 74.6 ng N m^{-2} s^{-1}) indicate that further field measurements are still needed.

In this study, the exchange fluxes of NO_X, NH_3 and N_2O between two typical Chinese agricultural fields and the atmosphere were investigated in the YRD in 2004 and in the NCP during 2008-2009. The influencing factors, the gas emission rates, and N fertilizer loss rates to N_2O, NO_X and NH_3 were determined.

Experimental Section

Sampling Site in the YRD

The sampling site was Shuangqiao farm (30º50'N, 120º42'E), about 10 km north of Jiaxing city, Zhejiang province, China. The farm consisted of an area of about 40 ha. The soil was classified as Typic Endoaquepts with NO_3^- -N of 4.29 mg kg^{-1}, $NH4^+$-N of 12.1 mg kg^{-1}, total N of 1.9 g kg^{-1}, and pH of 6.12 (in a 1:2.5 soil-to-water ratio). The experimental area was about 667 m^2 (divided into two

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

sampling plots) for investigating NO_x and NH_3 exchange fluxes from winter wheat in 2004. One plot (UC) was traditionally fertilized with urea and the other (UL) was fertilized by using a mixture of urea and lignin (lignin was from the sewage of paper production). It has been reported that N fertilizers with added lignin could increase the yield of crops (*39*). However, there are no studies that have examained the influence of lignin on the emission of NO_x and NH_3. A small area of bare soil in the UC plot was used as a control (CS). Prior to winter wheat sowing, both plots received 400 kg ha^{-1} compound fertilizer ($N:P_2O_5:K_2O$ = 20%:10%:10%) as basal fertilizer while urea (70 kg N ha^{-1}) was applied to each plot on 29 February, 2004. All fertilizers were surface broadcast. In order to study the effect of lignin on the emissions of NO_x and NH_3, an aqueous solution of urea (105 kg N ha^{-1}) was applied to the UC and CS plot before the tassel stage (8 April, 2004). The UL plot was fertilized with a mixture of urea and lignin (10/1, w/w). Seasonal variations of NO_x and NH_3 fluxes were measured between March 5 and June 1, 2004. Average sampling frequency was approximately 2 days between 12:00 to 16:00. The wheat was sown on 15 December 2003 and harvested on 28 May, 2004 (149th day). Rice was cultivated in the same experimental manner as wheat, and two treatments were included: conventionally fertilized (RF) and no fertilizer input (RN) plots. The rice was transplanted on July 6, 2004. Compound fertilizer (300 kg ha^{-1}, $N:P_2O_5:K_2O$ = 20%:10%:10%) was applied as basal fertilizer to RF plot. On July 15 and August 30, 2004, urea was side-dressed to the RF plot at the rates of 69 and 51.7 kg N ha^{-1}, respectively. The rice was harvested on October 30, 2004.

Sampling Site in the NCP

The field experiment was carried out in an agricultural field (38°71′N, 115°15′E) in Wangdu County, Hebei Province, China. The investigated crops were wheat (*Triticum aestivum* L.) and summer maize (*Zea mays* L.) under rotational cultivation. The field soil was classified as Aquic Inceptisol with a sandy loam texture. Soil pH (in a 1:2.5 soil-to-water ratio) was 8.1, the soil organic C was 8.34-9.43 g kg^{-1} and total N was 1.02-1.09 g kg^{-1}. The annual mean rainfall is about 555 mm and annual mean temperature is about 12.3 °C. The highest and lowest monthly mean air temperatures are 26.5 °C in July and -4.1 °C in January.

The experimental field with a total area of 68 m^2 was divided into three 6.5×3.5 m^2 plots, including control (CK, without crop, fertilization and irrigation), fertilizer N (NP) and wheat straw incorporated plus fertilizer N (SN) treatments. Maize was sown on 25 June, 2008, and 29 June, 2009. According to the cultivating methodology of local farmers, compound fertilizers (525 kg ha^{-1}, $N:P_2O_5:K_2O$ = 17%:20%:8% in 2008 and 413 kg ha^{-1}, $N:P_2O_5:K_2O$ = 24%:12%:6% in 2009) as basal fertilizer were evenly broadcasted onto the soil surface by hand after sowing for all plots. Another kind of compound fertilizer (375 kg ha^{-1}, $N:K_2O$ = 22%:8%) was further applied to the NP and SN plots as supplementary fertilizer on 16 August, 2008, and urea (150 kg ha^{-1}, N = 46.2%) as supplementary fertilizer was applied to the NP and SN plots on 1 August, 2009. Wheat straws (9.5 t ha^{-1} in 2008 and 4.3 t ha^{-1} in 2009, N = 0.48%) were evenly broadcast onto the soil surface as basal fertilizer in the SN plot in both years. Flooding was initiated immediately after the application of supplementary fertilizer in 2008 and basal fertilizer in 2009. The field was not irrigated on 25 June, 2008, and 1 August, 2009, due to strong rain events with cumulative rainfall of ~25 mm. Maize was harvested in mid-October for both years.

Measurements of N_2O, NO_X and NH_3 Fluxes

For the winter wheat and paddy fields in the YRD, NO_X and NH_3 fluxes were measured by dynamic chambers and the concentrations of NO_X and NH_3 were measured by the national standard methods for environmental air pollution in China (*39*). N_2O fluxes from the maize field in NCP were investigated by static chambers, and NO_X and NH_3 fluxes were measured by dynamic chambers. N_2O concentration was measured by our improved GC-ECD method (about 0.1% CO_2 in N_2 was introduced into the ECD as makeup gas) and the concentrations of NO_X and NH_3 were measured by a chemiluminescent NH_3 analyzer (Thermo Electron model 17i, USA). Detailed information about the chambers and flux measurements can be found in other published reports (*40–44*).

Results and Discussions

NO_X and NH_3 Fluxes from the Winter Wheat and Paddy Field in the YRD

Figure 1 shows the seasonal variations of NO_X and NH_3 fluxes from the winter wheat and paddy field in 2004. For NO, the average fluxes from the UC (urea only) plot were 79 and 3.7 ng N m^2 s^{-1} for winter wheat and rice, respectively. The majority of NO was emitted during the winter wheat growing period. An exponential dependence of NO fluxes on soil temperature was observed during the main growing period of winter wheat ($r = 0.76$, UC, $p<0.01$), suggesting that soil temperature was the key factor affecting NO fluxes (*27*, *45*).

The pathway of NO emission from rice fields is either through the rice plants or the soil/water interface. NO emission from the soil/water surface would result in a negative correlation between NO fluxes and ambient concentrations in soil/water. However, the correlation coefficient was less than 0.32 ($P < 0.02$, $n = 53$). Thus the main pathway of NO emissions from the flooded rice fields appear to be from rice plants (*46*). Non-flooded drained fields favor NO production by nitrification at surface soil which can easily escape into the atmosphere.

The average fluxes from the UL plot (urea and lignin) were 160 and 3.2 ng N m^{-2} s^{-1} for winter wheat and rice, respectively. Previous studies (*47–50*) indicated that lignin or polyphenols had a strong influence on determining the availability and release of N which might result in little immediate mineralization, thereby likely lowering N_2O emissions. Since NO and N_2O emissions from soil mainly come from the microbial activity through the processes of nitrification and denitrification (*51*, *52*), addition of lignin might also inhibit NO emission. Contrary to our expectation, addition of lignin to the wheat field greatly increased NO emission rates in this study. The mechanism for lignin inducing NO emission requires further study.

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

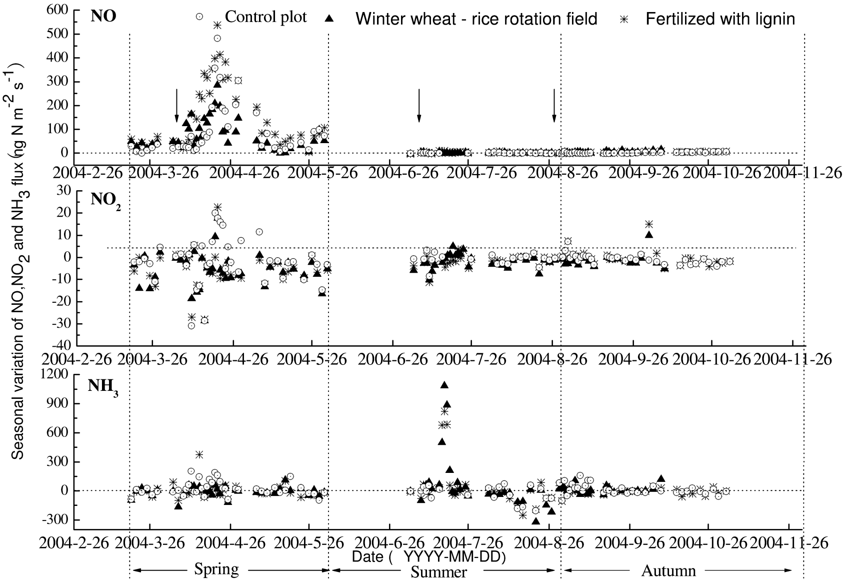


Figure 1. NO, NO_2, and NH_3 fluxes from the winter wheat and paddy field in the YRD in 2004. The arrows indicate time of fertilizer application.

In contrast to NO fluxes, NO_2 fluxes for the three plots were mostly negative except for a few days after fertilization. The average flux from the UC plot was -5.6 ng N m^{-2} s^{-1} with low emissions after fertilizer application. The emission is thought to be a result of below canopy chemical production of NO_2 (via the NO + O_3 reaction) rather than a plant physiological effects (*53*). NO_2 fluxes show negative correlations ($r = 0.67$, $P<0.05$, $n = 93$) with ambient concentrations for the entire period of data collection. Ambient concentrations were a key factor influencing NO_2 flux. The compensation point (CP) of NO_2 over UC plot could be derived from correlation as 5.2 µg m^{-3}, which was close to that (4 ppbv) for a canopy of orchard reported by Walton et al. (*53*).

Previous studies (*54–56*) indicated that NH_3 exchange flux above soil depends on many factors such as soil NH_4^+-N content, pH, moisture, temperature and fertilizer application. It is reported that NH_3 can either be emitted from soils and plants or be deposited to soils and plants (*57*, *58*). The field (UC) investigated in this study was both a source and a sink with average NH_3 fluxes of -5.1 and 19.3 ng N m^2 s^{-1} for winter wheat and rice, respectively. Therefore, the rice field could be considered a source for atmospheric NH_3, especially after 15 July, 2004, when the NH_3 fluxes increased sharply for three days after fertilizer application. By subtracting the value from the CS plot, the N loss as NH_3 for the UC plot was 3.5%, which is much lower than that reported for rice fields in northern China. This difference was ascribed to different pH values between Northern (pH = 8.4~8.8) and Southern (pH < 6.5) China soils.

Average NO_X and NH_3 fluxes from the winter wheat/rice field are provided in Table I. The averaged fluxes show the field in this area of China acts as strong emission source for atmospheric NO and smaller sink of NO_2. The lignin added to fertilizer (10/1, w/w) could increase the corn yield by about 15%. However, the N loss from the UL plot was about 54.5% larger than UC plot. The total area of winter wheat and rice in this area were 6.86×10^6 ha and 8.66×10^6 ha, respectively (*59*). Assuming the UC plot flux represented the average value from a corn field in the YRD, the total emission of NO from the winter wheat field and the rice field would be 35 Gg N and 3.5 Gg N, respectively. The yearly emission of NO from the winter wheat–rice rotation field would be about 38.5 Gg N and accounted for about 5.9% of the total gaseous N emissions in China (657 Gg N, (*60*)).

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

N_2O Exchange Fluxes

N_2O emissions from the CK plot during two maize growing periods are shown in Figure 2a. Small pulse emissions of N_2O were only observed after rain events on 24-28 June in 2008. Several pulse emissions occurred after corresponding rain events in 2009, especially the abruptly remarkable increase of N_2O emission (from 10 to 312 ng N m^{-2} s^{-1}) after the rain event on 8 July, 2008. Compared with 2008, less frequent rainfall events occurred from June to mid-July in 2009. The influence of soil moisture on N_2O emission has been well recognized and is more prominent after rewetting of extremely dry soil (*61*). Therefore, the sharp increase of N_2O emissions were ascribed to the rewetting of dry soil (WFPS<20%, Figure 2a). Except for the rainfall episode on 8 July, 2009, the pulse N_2O emissions from the CK plot from other rainfall events, in both years, were relatively insignificant. This was probably ascribed to the relatively high soil moisture (usually greater than 35%, Figure 2a) before specific rainfall events. It should be mentioned that the background N_2O emissions in this study might be largely overestimated because of artificial change of the soil moisture in the CK plot (without plants). Excluding the pulse N_2O emissions due to the rainfall events, the average N_2O fluxes in 2008 and 2009 were 7.20 and 10.3 ng N m^{-2} s^{-1}, respectively. These values were at the upper limit of the reported range (0.317-8.02 ng N m^{-2} s^{-1}) for the background N_2O emissions from croplands in China (*62*).

N_2O emissions from the NP and SN plots during two maize growing periods are presented in Figure 2b and 2c. In general, fertilizer application combined with irrigation greatly stimulated N_2O emission for a duration of about 10 days. The cumulative N_2O emissions during the experimental periods accounted for 70-90% of the total emission from each fertilization plot during the two maize growing seasons. The average N_2O fluxes from NP and SN plots were 72.1 and 76.6 ng N m^{-2} s^{-1} in 2008, and 30.0 and 35.0 ng N m^{-2} s^{-1} in 2009, respectively. The EFs from the NP and SN plots were 3.78% and 3.18% in 2008, and 1.08% and 1.20% in 2009, respectively.

Table I. Average fluxes and the crop yield from different plots

Period	*Plot*	*N*	*NO (ng N m^{-2} s^{-1})*	*NO_2 (ng N m^{-2} s^{-1})*	*NH_3 (ng N m^{-2} s^{-1})*	*∑N (ng N m^{-2} s^{-1})*	*Yield (kg ha^{-1})*
Winter wheat	UC	40	79	-5.6	-5.1	68.3	275
	UL	40	160	- 5.7	2.8	157.1	396
Rice	UC	62	3.7	-1.7	35.4	37.4	597
	UL	62	3.2	-0.9	22.2	24.5	607
Totally average	UC	102	33.3	-3.2	19.3	49.4	872
	UL	102	64.5	-2.8	14.6	76.3	1003

N_2O, NO_X, and NH_3 fluxes from the maize field in the NCP.

The fertilizers applied to NP and SN plots were 2.4%-15% more in 2008 than in 2009. The N_2O emissions from the two plots in 2008 were higher than those in 2009 by a factor of 2. The replicated measurements during the two maize seasons revealed that the spatial variations in each plot were usually less than 37% when N_2O fluxes were greater than 30 ng N m^{-2} s^{-1}. It is evident that the amount of N fertilizer application and the spatial variation could not explain the significant yearly variation. Since the soil temperature, NO_3^--N, and NH_4^+-N content in both years were almost identical or lower in 2008 (data not shown), the large difference between the two years was suspected to be the different soil moistures (e.g. the WFPS was 70-90% in 2008 while 50-70% in 2009). As reported by Davidson (*63*), Granli and Bøkman (*64*) and McTaggart et al. (*65*), nitrification and denitrification have been recognized as the main N_2O production processes in soil, and the favorable WFPS levels for nitrification and denitrification generally occur at 30-70% and 70-90%, respectively. Some field studies revealed that denitrification was the dominant process for N_2O emission from various croplands (*66*, *67*). Therefore, the extremely high N_2O emissions from the NP and SN plots in 2008 compared to 2009 were probably due to the soil moisture level which favored denitrification.

The cumulative N_2O emissions from the SN plot were 6.6% in 2008 and 16.4% in 2009 more than those from NP plot. The slightly higher N_2O emissions from the SN plot during the two maize growing periods were probably ascribed to additional N from wheat straw. Additionally, the high oxygen demands following straw amendments were conducive to denitrification.

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

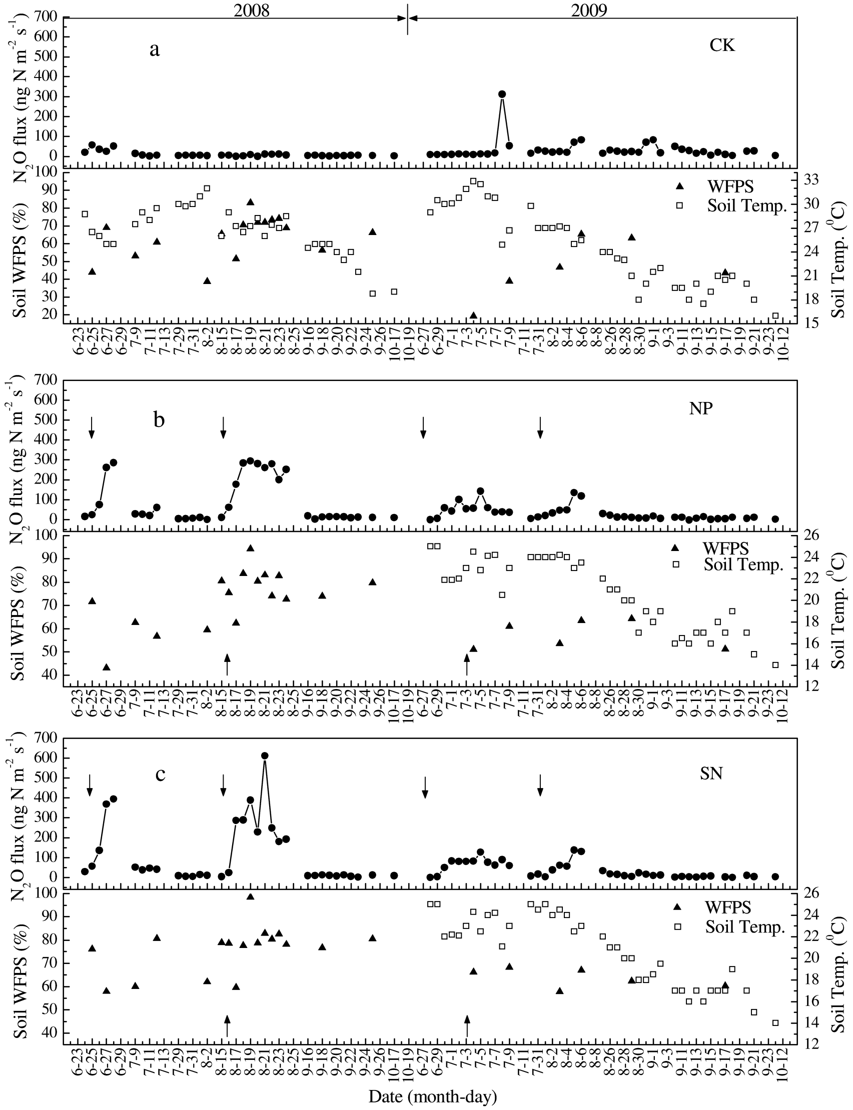


Figure 2. Variations of N_2O flux, soil water-filled pore space (WFPS) and soil temperature from CK (a), NP (b) and SN (c) plots during the two maize growing periods. Downward facing solid arrows show fertilizer applications; upward facing solid arrows show irrigation events. (Journal of Environmental Sciences -China, 2011, accepted)

NO_X Exchange Fluxes

NO_X emissions from the NP and SN plots also increased following fertilizer application. The duration of the pulse emissions induced by basal fertilization was also about 10 days (Figure 3a and 3b). The highest NO emission rate (~1100 ng

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

N m^{-2} s^{-1}) from the NP plot was about 3 times higher than that (340 ng N m^{-2} s^{-1}) from SN plot after the basal fertilization. There was no significant difference between the two plots after the supplementary fertilizer application (~350 ng N m^{-2} s^{-1}). A possible explanation was that the fresh wheat straw in the SN plot could consume oxygen in the soil. Consequently, any NO formed in the soil would be easily consumed by denitrifiers (*68*). The wheat straw had degraded considerably at the time of supplementary fertilizer application and its influence on soil oxygen became less important. Several investigators found pulses of NO emission when dry soil became wet (*69*, *70*). This effect of soil moisture change on NO emissions has been incorporated into statistical and empirical models for estimating NO emissions from soil (*16*, *19*). In this study, a small pulse emission (from -7.85 to 34.6 ng N m^{-2} s^{-1}) of NO from the CK plot was observed after the rain event on 8 July, 2009.

The average NO fluxes were 1.08±0.46, 36.5±13.2 and 16.7±5.67 ng N m^{-2} s^{-1} for CK, NP and SN plots, respectively. Fertilizer loss rates as NO-N were 1.93% for the NP and 0.76% for the SN plots. It is evident that field incorporation of straw could greatly reduce NO emission (~54%). The NO loss rates obtained by this study were in the range for different types of soils with different plants reported in other studies (0.003%-11%, (*71*)).

NO_2 emissions were only observed from the NP and SN plots after fertilization. Significant correlation between NO and NO_2 fluxes (R = 0.67-0.81, N = 38, P<0.01) were found for the three plots. These findings indicate that NO_2 emissions were mainly ascribed to photochemical conversion of NO to NO_2 in the dynamic chamber. The average NO_2 fluxes during the maize growing period (late June-October) were 0.81±0.52, 4.13±2.84 and 0.22±2.13 ng N m^{-2} s^{-1} for CK, NP and SN plots, respectively.

NH_3 Exchange Fluxes

Two emission peaks of NH_3 were observed from the NP and SN plots on 2 July, 2009, and from the NP plot on 2 August, 2009 (Figure 3c). Differing from NO, the first NH_3 emission peaks from the two plots were almost identical and the second NH_3 peak (only observed from the NP plot) was within a one-day duration. The relatively low NH_3 emissions after supplementary fertilization from the SN plot coincided with the relatively low NH_4^+ concentration in the soil (data not shown). The average NH_3 fluxes were -23.8±4.56, 94.0±45.3 and 15.2±44.1 ng N m^{-2} s^{-1} for CK, NP and SN plots, respectively. It is evident that field straw incorporation into the soil can greatly reduce NH_3 emission by ~84%.

With exception of the pulse emission induced by fertilization, the investigated field always acted as a small sink for atmospheric NH_3. The fertilizer loss rates as NH_3-N were calculated based on the data during the two emission periods (30 June-7 July, 2009, for basal fertilizer application and 2-5 August, 2009, for supplementary fertilizer application): losses were 5.24% and 3.03% for the NP and SN plots, respectively. Compared with the basal fertilizer application, significantly low NH_3 emissions after the supplementary fertilizer application indicated that the maize crop could absorb large portions of NH_3 emitted from the soil.

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

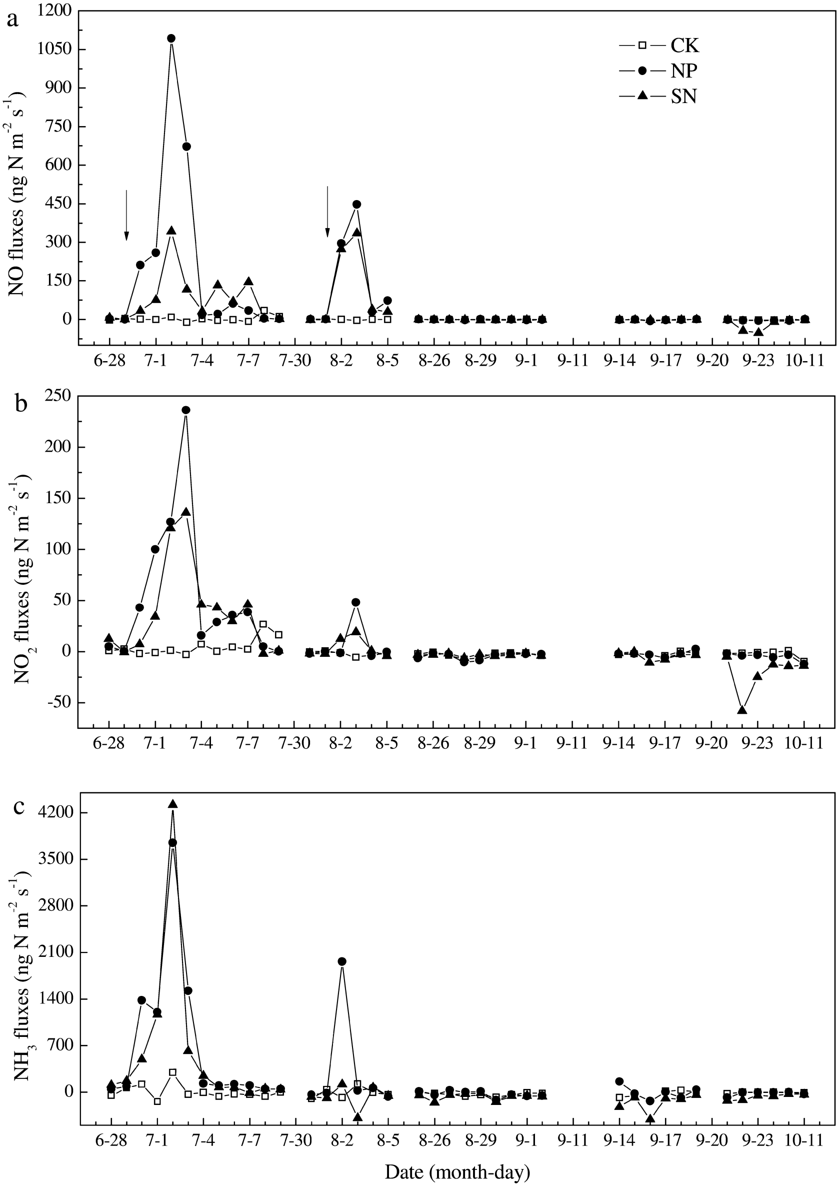


Figure 3. Variations of NO (a), NO_2 (b) and NH_3 (c) fluxes from the three treatments during the maize growing period in 2009. Arrows show fertilizer applications. (Atmospheric Environment, 2011, 45:2956-2961)

Origins of N_2O and NO Emissions

The formation of N_2O and NO in agricultural soils has been attributed to be a microbial mediated nitrification and denitrification process. However, detailed

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

information about the dominant process in most agricultural fields is still unclear. The ratio of NO/N_2O is being used as a potential methodology for distinguishing soil nitrification and denitrification (*72–74*). Anderson and Levine (*72*) found the molar ratio of NO/N_2O was usually greater than unity for nitrifiers and much less than unity for denitrifiers. From field measurements, however, Meijide et al (*74*) found the predominance of nitrification occurred when NO/N_2O>0.11. In this study, 64% of ratios of NO/N_2O from NP and SN treatments were less than unity, and the ratios less than 0.11 accounted for 39% from NP and 52% of SN, respectively. For the CK plot, 72% of NO/N_2O ratios were less than 0.11. The higher percentage of ratios <0.11 in the SN plot as compared to the NP plot was ascribed to the wheat straw consuming oxygen which favored denitrification. The significantly lower percentage of NO/N_2O<0.11 in the NP and SN plots than that in the CK plot was primarily due to fertilizations. Therefore, N_2O emissions during most of the maize growing period might be dominated by denitrification. Because the largest proportions of N_2O (>80%) and NO (>95%) emitted from the NP and SN plots during the periods after fertilization when the ratios of NO/N_2O were greater than unity (Figure 4), nitrification directly contributed to NO and N_2O emissions from the investigated maize field.

Environmental Implications

Maize is cultivated in this region during June-October when the photochemical reactions are the most active. Because the formation of photochemical oxidants (such as O_3) in rural areas is usually limited by NO_X (*75*), the strong NO pulse emissions induced by fertilization would greatly elevate atmospheric O_3 levels over a large region. Such emissions can impact the air quality of a large city such as Beijing and Tianjin. To effectively mitigate O_3, the authors propose reducing NO_X emissions from agricultural fields in the NCP region.

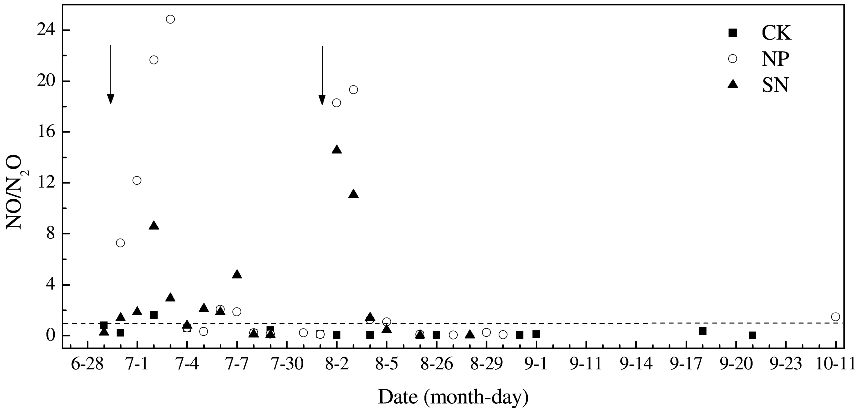


Figure 4. Molar NO/N_2O ratios from CK, NP and SN plots during the maize growing period. Arrows show fertilizer applications. The intercept of the dash line on the Y-axis represents the molar ratio of NO/N_2O equated to unity. Arrows show fertilizer applications. (Atmospheric Environment, 2011, 45:2956-2961)

A large fraction of the emitted NH_3 from the maize field in this region can be quickly converted to ammonium as fine particles via heterogeneous reactions on acid particles or photochemical reactions. The fine particle of ammonium is readily soluble, and can greatly reduce atmospheric visibility via absorption of atmospheric water vapor. Although the duration of the pulse emission of NH_3 induced by fertilizer lasted for several days, the long lifetime of atmospheric ammonium as fine particles can pose a problem since they are more persistent for a much longer time and over a larger region. The high frequency of haze-days in the NCP in recent years is closely relating to the high concentration of fine particles in which ammonium accounted for the largest proportion of the total cations (*76*). Zhang et al (*77*) recently calculated agricultural ammonia emissions inventory in the NCP, and found that 54% of the total emission (3071 kt NH_3-N yr-1) was from mineral fertilizer application. Therefore, to improve the air quality in the NCP, mitigating NH_3 emission from the agricultural region is urgently needed.

Conclusions

With the exception of the rice field, the investigated agricultural fields both in the YRD and NCP were large sources of atmospheric NO_X. The rice field in the YRD and the maize field in the NCP were important sources for atmospheric NH_3. The maize fields in the NCP were strong sources for atmospheric N_2O. The N emissions from the investigated fields were mainly ascribed to fertilization. Nitrification was recognized as the dominant process for contributing NO and N_2O emissions from the maize field in the NCP.

Acknowledgments

This work was financially supported by a Special Fund for Environmental Research (201009001), the Chinese National Natural Science Foundation (41075094, 40830101 and 20977097), the National Water Special Project (2008ZX07421-001 and 2009ZX07210-009), the Chinese Academy of Sciences (KZCX2-YW-Q02-03), and National Basic Research and the Development Program 973 (2010CB732304).

References

1. Khalil, M. I.; Schmidhalter, U.; Gutser, R. *Water, Air, Soil Pollut.* **2006**, *175*, 127–148.
2. Crutzen, P. J. *Q. J. R. Meteorol. Soc.* **1970**, *96*, 320–325.
3. Cicerone, R. J. *Science* **1987**, *237*, 35–42.
4. Intergovernmental Panel on Climate Change (IPCC). *IPCC Third Assessment Report: Climate Change 2001, the Scientific Basis*; Cambridge University Press: Cambridge, 2001.
5. Crutzen, P. J. *Annu. Rev. Earth Planet. Sci.* **1979**, *7*, 443–472.

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

6. Aneja, V. P.; Blunden, J.; James, K.; Schlesinger, W. H.; Knighton, R.; Gilliam, W.; Jennings, G.; Niyogi, D.; Cole, S. J. *Environ. Qual.* **2008**, *37*, 515–520.
7. Brasseur, G. P.; Orlando, J. J.; Tyndall, G. S., Eds.; *Atmospheric Chemistry and Global Change*; Oxford University Press: New York, 1999.
8. Roclofs, J. G. M.; Boxman, A. W.; VanDijk, H. F. G. In *Effect of Ammonium on Natural Vegetation and Forest*; Asman, W. H., Diederen, H. S. M. A., Eds.; 1987; pp 266–276.
9. Jambert, C.; Serça, D.; Delmas, R. *Nutr. Cycling Agroecosyst.* **1997**, *48*, 91–104.
10. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. *Global Biogeochem. Cycles* **2002**, *16*, 1024.
11. Sehy, U.; Ruser, R.; Munch, J. C. *Agric., Ecosyst. Environ.* **2003**, *99*, 97–111.
12. Li, D. J.; Wang, X. M. *Atmos. Environ.* **2007**, *41*, 9498–9505.
13. Li, D. J.; Wang, X. M. *Atmos. Environ.* **2008**, *42*, 4747–4754.
14. Mosier, A.; Kroeze, C.; Nevison, C.; Oenema, O.; Seitzinger, S.; vanCleemput, O. *Nutr. Cycling Agroecosyst.* **1998**, *52*, 225–248.
15. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. *Global Biogeochem. Cycles* **2002**, *16*, 1080.
16. Yienger, J. J.; Levy I, H. J. *Geophys. Res.* **1995**, *100*, 11447–11464.
17. Davidson, E. A.; Kingerlee, W. *Nutr. Cycling Agroecosyst.* **1997**, *48*, 37–50.
18. Lee, D. S.; Köhler, I.; Grobler, E.; Rohrer, F.; Sausen, R.; Gallardo-Klenner, L.; Olivier, J. G. J.; Dentener, F. J. *Atmos. Environ.* **1997**, *31*, 1735–1749.
19. Yan, X. Y.; Ohara, T.; Akimoto, H. *Global Biogeochem. Cycles* **2005**, *19*, GB3019.
20. Ding, W. X.; Cai, Y.; Cai, Z. C.; Yagi, K.; Zheng, X. H. *Sci. Total Environ.* **2007**, *373*, 501–511.
21. Colby, W. H.; Crook, F. W.; Webb, S. E. *Agricultural Statistics of the People's Republic of China. 1949–1990*; U. S. Department of Agriculture; Washington, D.C., 1992; p 106.
22. FAO. *Fertilizer*; FAO Yearbook, 1998, 48.
23. Ye, L. Q.; Guo, D. *China Statistical Yearbook*; China Statistics Press: Beijing, China (in Chinese), 2007.
24. Cao, J. L.; Tian, G. M.; Ren, L. T.; Cai, Z. C.; He, R. H. *J. Nanjing Agric. Univ.* **2000**, *23*, 51–54.
25. Walsh, M. Ph.D. thesis, Colorado State University, Fort Collins, CO, 2001.
26. Cai, G.; Chen, D.; White, R. E.; Fan, X. H.; Pacholski, A.; Zhu, Z. L.; Ding, H. *Aust. J. Soil Res.* **2002**, *40*, 737–748.
27. Zheng, X. H.; Huang, Y.; Wang, Y.; Wang, M. *Global Change Biol.* **2003**, *9*, 219–227.
28. Wang, Z. H.; Liu, X. J.; Ju, X. T.; Zhang, F. S.; Malhi, S. S. *Commun. Soil Sci. Plant Anal.* **2004**, *35*, 2917–2939.
29. Zhang, Y. M.; Chen, D. L.; Zhang, J. B.; Edis, R.; Hu, C. S.; Zhu, A. N. *Pedosphere* **2004**, *14*, 533–540.

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

30. Wang, S. B.; Song, W. Z.; Su, W. H.; Zeng, J. H.; Wang, Z. P.; Zhang, Y. M. *Rural Eco-Environ.* **1994**, *10,* 12–14 (in Chinese).
31. Zou, G. Y.; Zhang, F. S.; Chen, X. P.; Li, X. H. *Soil Environ. Sci.* **2001**, *10,* 273–276 (in Chinese).
32. Dong, Y.; Scharffe, D.; Qi, Y. C.; Peng, G. B. *Tellus, Ser. B.* **2001**, *53*, 1–9.
33. Dong, Y. H.; Ouyang, Z.; Li, Y. S.; Zhang, L. *J. Agro-Environ. Sci.* **2005**, *24,* 913–918 (in Chinese).
34. Ding, H.; Cai, G. X.; Wang, Y. S.; Chen, D. L. *Agric. Sci. China* **2002**, *1*, 184–188.
35. Meng, L.; Ding, W. X.; Cai, Z. C. *Soil Biol. Biochem.* **2005**, *37*, 2037–2045.
36. Zou, J. W.; Huang, Y.; Lu, Y. Y.; Zheng, X. H.; Wang, Y. S. *Atmos. Environ.* **2005**, *39*, 4755–4765.
37. Sun, Y. L.; Lu, P. L.; Li, J.; Yu, Q.; Sun, S. B.; Wang, J. S.; Ouyang, Z. *China J. Agrometeorology* **2008**, *29,* 1–5 (in Chinese).
38. Wang, Y. Y.; Hu, C. S.; Cheng, Y. S.; Zhang, Y. M.; Ming, H.; Yang, P. P. *J. Agro-Environ. Sci.* **2009**, *28,* 1508–1515 (in Chinese).
39. Mu, H. Z.; Zeng, W.; Huang, Y. C.; Sun, F. F. *Agro-Enviro. Prot.* **2000**, 18 (6), 251−253 (in Chinese).
40. Fang, S. X.; Zhang, Y.; Mu, Y. J. *J. Environ. Sci. (Beijing, China)* **2006**, *18*, 689–700.
41. Fang, S. X.; Mu, Y. J. *Atmos. Environ.* **2006**, *40*, 6329–6337.
42. Fang, S. X.; Mu, Y. J. *Atmos. Environ.* **2007**, *41*, 4766–4772.
43. Pang, X. B.; Mu, Y. J.; Lee, X. Q.; Fang, S. X.; Yuan, J.; Huang, D. K. *Atmos. Environ.* **2009**, *43*, 2571–2578.
44. Zhang, Y.; Liu, J. F.; Mu, Y. J.; Pei, S. W.; Lun, X. X.; Chai, F. *Atmos. Environ.* **2011**, *45*, 2956–2961.
45. Williams, E. J.; Hultchinson, G. L.; Fehsenfeld, F. C. *Global Biogeochem. Cycles* **1992**, *6*, 351–388.
46. Yu, K. W.; Wang, Z. P.; Chen, G. X. *Biol. Fertil. Soils* **1997**, *24*, 341–343.
47. Fox, R. H.; Myers, R. J. K.; Vallis, I. *Plant Soil* **1990**, *129*, 251–259.
48. Handayanto, E.; Cadisch, G.; Giller, K. E. *Plant Soil* **1994**, *160*, 237–248.
49. Millar, N.; Baggs, E. M. *Soil Biol. Biochem.* **2004**, *36*, 935–943.
50. Palm, C. A.; Sanchez, P. A. *Soil Biol. Biochem.* **1991**, *23*, 83–88.
51. Bremner, J. M. *Nutr. Cycling Agroecosyst.* **1997**, *29*, 7–16.
52. Johansson, C; Gallbally, I. E. *Appl. Environ. Microbiol.* **1984**, *47*, 1284–1289.
53. Walton, S.; Gallagher, M. W.; Duyzer, J. H. *Atmos. Environ.* **1997**, *31*, 2915–2931.
54. Freney, J. R.; Simpson J. R.; Denmead, O. T. In *Gaseous Loss of Nitrogen from Plant-Soil Systems*; Freney, J. R., Simpson, J. R., Eds.; Martinus Nijhoff/Drw. Junk Publishers: The Hague, 1983; pp 1−32.
55. Nemitz, E.; Milford, C.; Sutton, M. A. *Q. J. R. Meteorol. Soc.* **2001**, *127*, 815–833.
56. Harrison, R. M.; Yamulki, S.; Goulding, K. W. T.; Webster, C. P. *J. Geophy. Res.* **1995**, *100*, 25923–25931.
57. Georgii, H. W.; Lenbard, L. *Pure Appl. Geophy.* **1978**, *116*, 385–392.

Downloaded by OHIO STATE UNIV LIBRARIES on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch004

58. Denmead, O. T.; Freney, J. R.; Simpson, J. R. *Soil Biol. Biochem.* **1976**, *8*, 161–164.
59. China Year Book. 2006. National Bureau of Statistics of China. http://www.stats.gov.cn/english/statisticaldata/yearlydata/.
60. Wang, Q. G.; Han, Z. W.; Higano, Y. *Environ. Pollut.* **2005**, *135*, 83–90.
61. Jørgensen, R. N.; Jørgensen, B. J.; Nielsen, N. E. *Soil Biol. Biochem.* **1998**, *30*, 545–546.
62. Gu, J. X.; Zheng, X. H.; Zhang, W. *Plant Soil* **2009**, *320*, 307–320.
63. Davidson, E. A. In *Biogeochemistry of Global Change, Radioactively Active Trace Gases*; Oremland, R. S., Ed.; Chapman & Hall: New York, 1993; pp 369–383.
64. Granli, T.; Bøkman, O. C. *Norwegian J. Agric. Sci. Supp.* **1994**, *12*, 1–128.
65. McTaggart, I. P.; Clayton, H.; Parker, J.; Swan, L.; Smith, K. A. *Biol. Fertil. Soils* **1997**, *25*, 261–268.
66. Dobbie, K. E.; Smith, K. A. *Eur. J. Soil Sci.* **2001**, *52*, 667–673.
67. Russow, R.; Spott, O.; Stange, C. F. *Soil Biol. Biochem.* **2008**, *40*, 380–391.
68. Conrad, R. *Microbiol. Rev.* **1996**, *60*, 609–640.
69. Scholes, M.; Martin, R.; Scholes, R.; Parsons, D.; Winstead, E. *Nutr. Cycling Agroecosyst.* **1997**, *48*, 115–122.
70. Martin, R. E.; Scholes, M. C.; Mosier, A. R.; Ojima, D. S.; Holland, E. A.; Parton, W. J. *Global Biogeochem. Cycles* **1998**, *12*, 81–91.
71. Yan, X. Y.; Shimizu, K.; Akimoto, H.; Ohara, T. *Biol. Fertil. Soils* **2003**, *39*, 45–50.
72. Anderson, I. C.; Levine, J. S. *Appl. Environ. Microbiol.* **1986**, *51*, 938–945.
73. Williams, P. H.; Jarvis, S. C.; Dixon, E. *Soil Biol. Biochem.* **1998**, *30*, 1885–1893.
74. Meijide, A.; Díez, J. A.; Sánchez-Martin, L.; López-Fernández, S.; Vallejo, A. *Agric. Ecosyst. Environ.* **2007**, *121*, 383–394.
75. Aneja, V. P.; Robarge, W. P.; Sullivan, L. J.; Moore, T. C.; Pierce, T. E.; Geron, C.; Gay, B. *Tellus, Ser. B.* **1996**, *48*, 626–640.
76. Sun, Y. L.; Zhuang, G. S.; Tang, A. H.; Wang, Y.; An, Z. S. *Environ. Sci. Technol.* **2006**, *40*, 3148–3155.
77. Zhang, Y.; Dore, A. J.; Ma, L.; Liu, X. J.; Ma, W. Q.; Cape, J. N.; Zhang, F. S. *Environ. Pollut.* **2010**, *158*, 490–501.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Chapter 5

Greenhouse Gas Emissions from Rice Cropping Systems

W. R. Horwath[*]

University of California Davis, Dept. of Land, Air & Water Resources,
One Shields Avenue, University of California, Davis, CA 95616
[*]E-mail: wrhorwath@ucdavis.edu

Rice cultivation is an important source of greenhouse gases (GHGs) that cause global warming. Rice systems contribute over 25% of total global anthropogenic methane (CH_4) emissions currently. In this chapter, a review of rice cropping systems is presented in context of GHG emissions and possible mitigation measures. Increasing atmospheric carbon dioxide (CO_2) has been shown in many cases to increase methane emissions in rice. In-season drainage can reduce methane emissions up to 80%. However, practices such as straw incorporation and organic matter amendments can increase methane emissions. Different rice cultivars and hybrids have varying effects on methane emission but results indicate selection to reduce methane emission should be an area of future research. Nitrous oxide (N_2O) emissions are generally low compared to methane in irrigated rice. In-season draining to mitigate methane emissions will increase nitrous oxide emissions, but current studies show that the overall warming potential is generally lowered.

Introduction

Rice culture can emit greenhouse gases (GHGs), such as methane (CH_4) and nitrous oxide (N_2O). Rice paddies are similar to wetland ecosytems where plants are adapted to flooded conditions. The flooded status produces anoxic or reduced environments that are especially conducive to the production and emissions of CH_4. Both CH_4 and N_2O are active in absorbing infrared radiation causing the

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

greenhouse effect associated with climate change (*1*). These gases originate from both biogenic and abiotic sources. Emissions from biogenic sources account for 70% of total emissions and include wetlands, rice paddies, livestock, waste treatment, landfills and termites (Table I). Non-biogenic sources include fossil fuel exploration, biomass burning, and geological sources.

A substantial portion of the daily food requirements of more than 2 billion people is met by rice (*2*). The rapidly growing world population will require that food production, particularly rice, increase by 50% of 1990 levels (*3*). However, rice yields have declined or stagnated over the last decade in some areas, especially Asia, where the gains in yield during the green revolution starting in the 1970's were significant. Global rice production (yield ha^{-1}) has increased by 19% from 1990 to 2009; but for the last 10 years, yield increases have only been 8% (*4*). Figure 1 shows increases in the human population, rice yields and yields expectations forecast in the year 2000 and 2010 to the year 2050 (*2*, *3*). The more recent yield forecast indicates the need for a linear increase in food production to meet the needs of the growing population. However, the increase in rice yields is slow despite gains in cultivar improvement, genetic modifications and fertilizer technology. The recent yield declines have been attributed to declining soil N availability even though application of N fertilizer have steadily increased over the last 30 years (*4*). The decline is thought in part to be attributed to the intensification of production using additional rice planting within year and across years leading to extended periods of soil saturation. Extended flooding regimes have been shown to exhibit binding of available N to decomposition products, such as lignin aromatics (*5*). This may require additional N ferilizer to maintain rice yield potential and could increase N_2O emissions. In contrast, in a temperate California rice system, where only one rice crop is grown annually, the addition of rice straw and summer and winter flooding has no long-term effect on N availability. However, this practice results in increased CH_4 emissions (*6*).

Climate change will also affect the efforts to maximize rice yield potential. Studies on rice production and GHG emissions show both positive and negative results of intensification. The objective of this chapter is to give an overview of CH_4 and N_2O processes and the factors and management practices that affect overall GHG emission in rice production.

Global Methane

Methane is the most abundant hydrocarbon in the atmosphere. The current global abundance of CH_4 is 1775 ppb giving a total atmospheric burden of approximately 5,000 Tg (*7*). The total global annual emission of CH_4 is about 553 Tg. As a GHG, CH_4 is responsible for about 21% of the total radiative forcing attributed to the major GHGs or 0.48 W m^{-2}. The total annual global CH_4 sink is 537 Tg resulting in an approximate net annual release of 16.5 Tg emission to the atmosphere. The major removal mechanism of methane from the atmosphere involves radical chemistry; when it reacts with the hydroxyl radical

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

(·OH), initially formed from water vapor broken down by oxygen atoms that come from the cleavage of ozone by ultraviolet radiation. The reaction occurs in the troposphere resulting in a methane lifetime of 8 to 10 years. Upland soils comprise about 6% of the sink for methane facilitated through microbial oxidation to CO_2. Observations from the prior decade suggested atmospheric concentration decline growth and stabilization of atmospheric CH_4 burden (*8*). However, recent evidence suggests there is a renewed growth in atmospheric CH_4 following almost a decade of decline (*9*).

The biogenic sources of CH_4 account for about 60% of its total emission. Approximately 1% of global net primary production (NPP) is converted to CH_4, of which half is oxidized to CO_2 by methanothrophs in the soil (*10*). Rice cropping systems account for about 15% of total global CH_4 annual emissions.

Global Nitrous Oxide

The N cycle is complex and involving a number of oxidation/reduction (redox) processes that convert dinitrogen (N_2) to ammonia (NH_3) further to nitrate (NO_3^-) and back to N_2. The various redox of the N cycle support the growth of a wide range of soil microorganisms through supplying alternate electron acceptors and the ability to produce amino building blocks to construct proteins. The incomplete reduction of NO_3^- produces nitrogen oxides (NO_x and N_2O). Of the major GHGs, N_2O is the most potent in terms of reflecting infrared radiation back into the lower atmosphere. The radiative forcing attributed to N_2O in the atmosphere represents about 7% of the major GHGs. It has increased markedly since the preindustrial era from 270 to 319 ppb corresponding to a global burden of about 1510 Tg N (*7*). The atmospheric burden of N_2O continues to increase by 0.25% annually. The main sink for N_2O is photochemical destruction or reaction with energetic oxygen produced by photodissociation of ozone in the stratosphere but the process is slow resulting in a mean lifetime of about 300 years.

Agricultural activities, such as increased N fertilizer use and biological N fixation represent the largest source of N_2O released to the atmosphere today. In addition, N deposition from industrial processes and urban areas undoubtedly contribute more N to soils. In the past, land use change resulting from conversion to agriculture likely released significant N_2O from mineralization of soil organic mater (SOM). Today, the emissions of N_2O from soil and fertilizer N applications represent more than 60% of total global emissions to the atmosphere (Table I). Approximately 1% of the fertilizer N applied to soils is emitted as N_2O (*7*). In traditional flooded rice systems, N_2O emissions are relatively low due to reduced nitrification activity, a process providing both source and substrate for nitrifier denitrification and denitrification. Today's agronomic practices for intensified rice production often include in-season draining events in order to manage pest and disease, which can also increase nitrification and N_2O emissions.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Table I. Global sources and sinks for methane and nitrous oxide[a]

Sources	***Tg CH_4 yr^{-1}***	***Tg N_2O-N yr^{-1}***
Natural sources		
Wetlands	188	
Termites	24.5	
Oceans	9.5	3.7
Geological sources	9.5	
Hydrates	4.5	
Soils		6.3
Atmospheric processes		0.6
Total Natural sources	**236**	**10.6**
Anthropogenic sources		
Ruminants	87	
Rice production	83	
Biomass burning	64.5	0.6
Landfills	42	
Fossil fuel production/distribution	41	1.0
Agriculture		4.6
Rivers, wetlands, coastal		1.7
Total anthropogenic	**317.5**	**7.9**
Total	**553**	**18.4**
Sinks		
Atmospheric removal	504.5	
Soil microbial oxidation	32	
Total sinks	**536.5**	
Atmospheric increase (yr^{-1})	**+16.5**	**+18.4**

[a] Adapted from Horwath 2007 (*16*) , and IPCC 2007 (*6*).

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

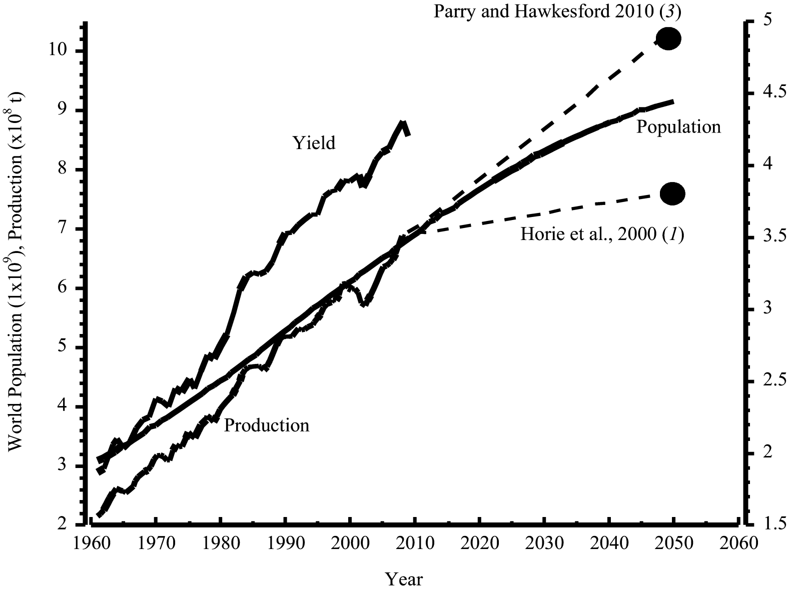


Figure 1. Projected population and rice yield and production increases to 2050. Filled circles represent projected rice needs in 2050. A 50% increase in yield will be required to meet food requirements of the growing population.

Biogeochemistry of Methane and Nitrous Oxide Production

Methogenesis

Methane is the end product of the breakdown of organic matter under anoxic or reduced conditions (*11*). It is formed directly from acetate or through the combination of hydrogen (H_2) and CO_2 by methanogens. The primary fermentation of complex (polysaccharides) and simple (sugars) organic compounds to alcohols and fatty acids is required to begin the process of CH_4 production. Methanogens cannot directly consume the primary fermentation products, which must be first converted to acetate, CO_2 and H_2 through secondary fermentation by a group of microorganisms called syntrophs (*12*). These organisms must work in concert or syntrophy with methanogens because they cannot complete the required secondary fermentation in the presence of excess H_2. As methanogens consume H_2 and CO_2 to produce CH_4, the syntrophic bacteria can continue to produce secondary fermentation products to drive the formation of CH_4 (Figure 2). Another physiologically distinct group of fermenting bacteria called the homoacetogens ferment sugars directly to acetate (*12*). The fermentation process occurs during the sequential reduction of electron acceptors following depletion of oxygen. The sequential reduction of NO_3^-, Mn(IV), Fe(III), sulfate (SO_4^{2-}) and finally CO_2 are required before CH_4 is produced (Figure 2). The production of CH_4 occurs at redox potentials of <-150 mV. The stoichiometry of CH_4 production from H_2 plus CO_2 ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$)

and acetate ($CH_3COOHC \rightarrow CH_4+CO_2$) is 1/3 to 2/3 in rice soils, respectively (*13*). Factors affecting the stoichiometry of CH_4 production include available C source, temperature and fertilizer practices.

Methane emission occurs through the rice plant, ebullition and diffusion (*14*). Greater than 90% of CH_4 emissions occurs through the aerenchyma cells of the rice plant. Ebullition during the flood period and mass flow release of CH_4 following draining of rice paddies for harvest results in 10 to 30% of total seasonal CH_4 emission (*6*).

Denitrification

The microbial reduction of NO_3^- to intermediate gases nitric oxide (NO) and N_2O and finally to N_2 is called denitrification. The microorganisms capable of denitrification are diverse and include the taxa *Pseudomonas*, *Bacillus* and *Thiobacillus*. Under anoxic conditions, NO_3^- is an alternate electron acceptor for heterotrophic microorganisms or facultative anaerobes at redox potentials ranging from 100 to 300 mV (Figure 1). Once NO_3^- is formed, it can be reduced to N_2 in low redox environments, such as soils with 60 to 80% or greater water filled pore space or saturated conditions found in rice fields. Nitrous oxide can also be formed during the oxidation of NH_3 or NH_4^+ in the nitrification process. During nitrification, the intermediate hydroxylamine (NH_2OH) is formed before nitrite (NO_2^-), which can lead to the production of N_2O through its chemical decomposition. In addition, some ammonia oxidizers (*Nitrosomonas europaea, Nitrosolobus spp., Nitrosospira spp., Nitrosococcus spp.*) are capable of reducing NO_2^- to N_2O and N_2 under oxic and anoxic conditions. These processes are called nitrifier-denitrification and occur under much drier soil conditions compared to conditions that trigger denitrification (*15*).

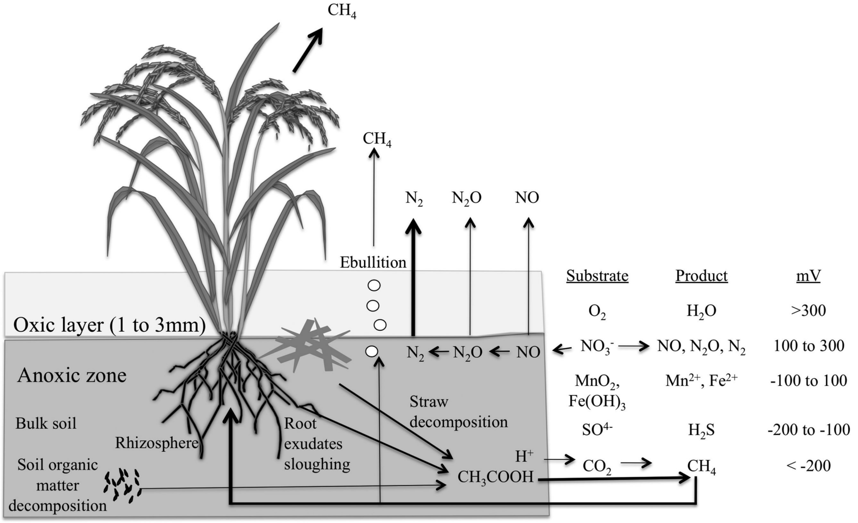

CH4
CH4
N2
N2O
NO
Ebullition
Oxic layer (1 to 3mm)
Anoxic zone
N2 ← N2O ← NO
← NO3- → NO, N2O, N2
Substrate
Product
mV
O2
H2O
>300
100 to 300
MnO2, Fe(OH)3
Mn2+, Fe2+
-100 to 100
SO4-
H2S
-200 to -100
CO2 → CH4
< -200
Bulk soil
Rhizosphere
Root exudates sloughing
Straw decomposition
H+
CH3COOH
Soil organic matter decomposition

Figure 2. Redox zones and processes affecting methane and nitrous emission in rice.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Spatial and Physical Characteristics of a Rice Paddy

Rice paddies are spatially delineated both vertically and horizontally by redox gradients. Vertical redox gradients are formed by the floodwater creating a barrier to atmospheric oxygen diffusion (Figure 2). Solum in rice paddies can be divided into 4 distinct zones of redox potential including rhizosphere, highly reduced bulk soil, slightly oxic soil surface and soil around rice residues (*16*). After flooding, it takes up to 3 weeks to reach a redox potential of less than -150mV needed produce CH_4 in both the rhizosphere and bulk soil. The length of time depends on the concentration of alternate electron acceptors in the soil and water column. After flooding, NO_3^- is quickly consumed and nitrification becomes negligible. A horizontal redox gradient develops around the roots from the diffusion of O_2 through the aerenchyma tissue of the rice plant. This makes the rhizosphere slightly less reduced than the bulk soil. The presence of O_2 in the rhizosphere creates the potential to oxidize CH_4, which appears to be negligible compared to the overall amount of CH_4 produced and subsequently diffused into the rice root. At the soil surface, an oxic layer forms from the diffusion of oxygen into the water column. The oxic layer on the soil surface acts to oxidize CH_4 diffusing from the soil into the water column making this loss pathway negligible under most circumstances. The reducing conditions in paddy soils can be increased following certain rice straw residue practices. In some systems where rice straw burning is banned or excessive rice straw is produced from multiple annual crops, leaving straw on the soil surface or incorporating it by plowing leads to increased microbial decomposer activity and significantly lower reducing conditions that increase overall CH_4 production (*6*).

Sources of Organic Matter for Methane Production

Available carbon (C) is needed as a substrate for both methanogens and denitrifiers. Available C is defined as the C easily decomposable and assimilated by rapid microbial growth and is directly related to CH_4 production (*6*). In a rice paddy, there are four main sources of C including: 1) root exudates and sloughing and turnover of roots, 2) straw 3) weeds and 4) SOM. Rice straw, weeds and SOM contribute a range of easily decomposable and resistant C fractions (*17*). The main source of readily decomposable C during the growing season are root exudates and root turnover consisting of simple compounds like sugars and amino acids. Straw also contains simple compounds like lipids, sugars and amino acids. The polysaccharide fraction of straw consisting of hemicellulose and cellulose is enzymatically broken down into simple sugars that provide easily assimilable substrates for reduction processes in rice paddies. Soil organic matter also contains easily degradable C in the light fraction, which consists of recently decomposing plant residues and microbial constituents (*17*). The contribution of the above fractions to CH_4 production is dependent on their quantities and state of decomposition.

In rice paddies, rice straw is the main source of C for CH_4 production during the early growth of rice when plants are small and the root system is in the establishment phase. Up to 98% of the total CH_4 emission in early season rice can be attributed to rice straw (*18*). As the growing season progresses, other sources of C are used in CH_4 production. The seasonal contribution of C sources to CH_4 production, determined using $^{13}CO_2$ labeling, was 42% rice straw, 37 to 40% rhizosphere deposition of exudates and sloughed roots and 18% to 21% SOM (*6*, *19*). When straw was removed from the rice paddy, the sources of C for CH_4 production was 80 to 85% rhizodeposition and 15 to 20% from SOM. A study done in a Mediterranean climate in California showed that winter flooding of rice paddies that contained rice straw from the previous season increased CH_4 emission four times compared to paddies where straw was removed (*6*, *20*).

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Factors Affecting Methane Emission in Rice Systems

Rice is the world's most important wetland food crop. Rice cropping systems include irrigated, rainfed, deep water and upland (*14*). The most common rice systems are irrigated followed by rainfed. Water levels are maintained between 5 to 20 cm in irrigated rice with developed water resources. Consistent flooding benefits rice by suppressing weeds and increasing nutrient availability especially P. In tropical rice where highly weathered soils can fix significant quantities of P, flooding produces reduced conditions that increase the solubility of phosphorus (P). In rainfed systems, rain events control the duration and depth of water with levels reaching 50 cm or greater. In deep water flooded systems, often located in riparian areas, flood depths vary from 50 cm to several meters. Greater than 90% of rice is grown under managed flooded conditions as water resources have been developed over the last decades. The maintenance of anoxic soil conditions is required to maximize yield, but leads to CH_4 emission. Upland rice is grown under unsaturated soil conditions and presently constitutes small portion of the global rice production area. Upland rice may become more common in the future to expand production because of water resource limitations expected from climate change and increasing human population.

Methane emission in rice is influenced by a variety of factors, but management practices, rice varieties and meteorological conditions are the most significant. Other site-specific factors include soil type, cropping intensity (crops per year), crop rotation and the use of organic amendments, particularly animal manures, crop residue and green manure. These variables interact to determine the potential of a given rice paddy to produce CH_4. There is sufficient understanding about these factors and their interactions to predict the occurance of CH_4 responses or events, but it is more difficult to predict the magnitude of the emission events (*21*, *22*). This limits the broad use of biogeochemical models at the field level.

Cultivar and Yield

The emissions of CH_4 are often directly related to the NPP of wetlands. As NPP increases to 10 to 12t ha^{-1}, CH_4 emissions increase up to 20 fold (*23*). Rice NPP of 12 to 20t of total biomass can rival *Typha spp.* wetlands in their capacity to produce and emit CH_4. Many studies have shown increasing CH_4 emission with increasing rice yield (Figure 3) (*24–26*). In contrast, it has been posited that

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

increasing rice yields can reduce CH_4 emission (*27*, *28*). However, the results graphed in Figure 3 do not generally support that increasing rice yields reduce CH_4 emission. The supposition that increasing yields reduce CH_4 emission is based on the assumption that increasing yield allocates more C to grain production leaving less to escape through rhizodeposition (*28*). This assumes the rice plant is C limited. It also suggests that management to optimize rice yield to create a grain C sink could reduce CH_4 emission and the authors suggest this to be an important aspect of variety and hybrid development.

Different rice cultivars can also affect CH_4 emission, but their influences vary in some cases from season to season and are difficult to evaluate. Rice cultivars that increase tillering (additional flowering shoots) have been shown to increase CH_4 emission (*29–32*). Increasing the number of shoots provides additional aerenchyma tissue to transport CH_4 from the soil to the atmosphere. An increase in total root weight has also been shown to increase CH_4 emission (*30*). Increasing root weight likely increases rhizodeposition and root sloughing providing available C to methanogens. Different rice varieties also have different capacities to conduct CH_4 to the atmosphere (*31*). These results suggest that rice varieties might be be selected to reduce overall CH_4 emission independent of other factors affecting CH_4 production.

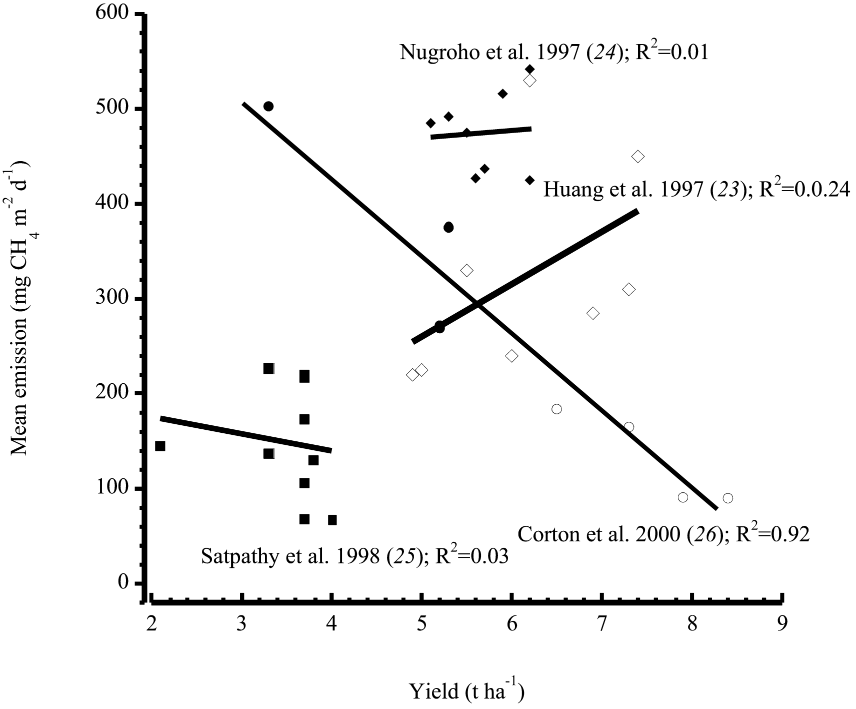


Figure 3. Relationship between rice yield and methane emission from various studies.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Other plant characteristics have also shown promise in reducing CH_4 production in the rhizosphere. High CH_4 emitting varieties were shown to have increased levels of root and rhizosphere glucose, fructose and acetic acid levels (*33*). The increase in available C compounds served as substrates for CH_4 production. However, the rhizosphere oxidation potential of hybrid rice was also found to be significantly higher than that for traditional varieties, despite similar CH_4 production potential and resulted in significantly lower CH_4 emissions (*34*). The authors attribute the lower CH_4 emission in hybrid rice to increased population of methanothrophs in the rhizosphere. The study provides evidence for possible cultivar and hybrid selection to modify soil microbial communities that increase the oxidation of CH_4 to CO_2 and reduce overall emissions. More research would be required to elucidate the underlying mechanisms and ascertain the selection of certain varieties over others with respect to their CH_4 emission potentials.

Soil Characteristics

A number of soil properties can affect CH_4 production. They include but are not limited to soil texture, mineralogy and soil organic matter content. Rice is often grown on heavier textured soils containing increased clay contents. The buffering capacity of soils can be directly related to CH_4 emission. Soils with rapid return of pH to neutral upon flooding decreased in redox potential more rapidly and hastened the onset of CH_4 production (*36*). Clay soils are generally more buffered than lighter textured soils and exhibit a prolonged onset to reduced conditions due to their increased content of alternate electron acceptors, such as Fe(III). Soil mineralogy and SOM content also impacts both the onset and maintenance of anoxic conditions by affecting the soil buffering capacity and plant growth. Methane emission increased from histosols (high organic matter) to gley soils (poorly drainage often heavy textured) to andosols (*35*). Methane emission from soils is positively correlated to the organic C and nitrogen (N) content (*36*). The same study also found that the depth of the organic matter in the soil surface layer was positively correlated to CH_4 emission. The more ordered structure found in clay soils may impede ebullition and increase CH_4 transport through rice aerenchyma cells (*24*).

Field Management

A number of field management practices affect CH_4 emissions. They include planting density, tillage, fertilizer types and application practices, organic mater amendments, and water management. These practices affect CH_4 emissions by altering the chemical and biophysical properties of the plant-soil system, and thus offer mitigation opportunities for reducing CH_4 emissions from rice cultivation. Table II presents a list of alternative management practices that may potentially reduce GHG emissions from rice paddies.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Table II. Summary of practices for CH_4 and N_2O mitigation potential

Mitigation Option	*Description*	*Reduction efficiency (%)*	*Reference*
Methane (CH_4)			
Midseason single drainage	Reduce anaerobic conditions	40[a],80[b]	(*38*, *39*)
Multiple drainage	Reduce anaerobic conditions	48[a],80[b]	(*38*, *39*, *56–58*)
Rice straw compost	Substitute for fresh rice straw; lowers organic matter	61[b]	(*38*)
Off-season straw incoporation	Prolong aerobic decomposition	50[b.c]	(*39*)
Phosphogypsum/ gysum	Inhibit methanogenesis	73[b]	(*38*)
Direct wet seeding	Replace transplanting;	54[b]	(*38*, *40*)
Ammonium sulfate with no drainage	Replace commonly used urea; sulfate inhibits Methanogenesis	36[b]	(*38*)
Iron addition	Inhibit methanogenesis	84[b]	(*38*)
Rice cultivar	Reduce gas transport	Inconsistent	(*34*, *40*, *41*)
No-tillage	Reduce disturbance of SOM	29[b]	(*45*, *46*)
Tile drainage	Improve soil oxidation	40[a,d]	(*42*)
Nitrous Oxide (N_2O)			
Nitrification inhibitor	Reduce nitrification	38[a],53[b]	(*37*, *38*)
Urease and nitrification inhibitor	Reduce hydrolysis of urea and nitrification	50[a]	(*37*, *38*)
Slow release fertilizer	Increase plant uptake of N	35[a],80[b]	(*37*, *38*)

[a] Average value. [b] Maximum value. [c] Modeling study. [d] Laboratory incubation study.

Planting Density

Rice planting practices can affect CH_4 emissions but few studies have been conducted in this area (*43*). High plant densities in a comparison of 19 cultivars stimulated CH_4 production in soil but did not increase overall CH_4 emission (*44*). The authors attributed this observation to higher oxygen transport to soil through the aerenchyma cells, stimulating CH_4 oxidation. In practice, promotion of tillering should be comparable to higher plant densities in providing conduits to the atmosphere via the aerenchyma cells. However, higher plant densities would increase the number of individual root systems and raise the oxic environment of the multiple rhizospheres under higher plant densities. Increased tillering would have a lower number of individual root systems but more shoots to conduct CH_4 in comparison to increased planting density.

Tillage Effects

Few studies of tillage impacts on CH_4 production in rice have been conducted. Tillage effects are normally not considered because soil flooding reduces the effects of physical disturbance on soil structure through soil puddling. However, tillage can alter the depth and placement of crop residues and organic amendments, which can alter the supply and spatial distribution of substrates for methanogens. In a study in central China, no-tillage resulted in a 22% decrease in CH_4 emission compared to conventional tillage and fertilization practices (*45*). In the same study with no N applied, conventional tillage increased CH_4 emission by 12% compared to no-tillage. In a study in Japan, no-tillage reduced CH_4 emission up to 29% compared to conventional tillage practices (*46*). Factors affecting CH_4 emission under no-tillage include changes in bulk density and placement of crop residues. Leaving rice straw on the soil surface in proximity to the narrow soil surface oxic layer may increase the oxidation of CH_4 despite the straw adding available C.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Fertilizer Management

Fertilizer N additions in rice can be as high as 250 kg ha^{-1} or higher to maximize yield potential. High N application can induce tillering, however it can cause lodging (laying over of the plant) which reduces quality and mechanical harvest yields. The type of fertilizer N can also impact CH_4 emission potential. In general, ammonium based fertilizers reduce CH_4 emission in comparison to organic amendments and nitrate base fertilizers (*47*). Ammonium based fertilizers stimulate methanothrophs leading to greater CH_4 oxidation to CO_2. The application of ammonium nitrate can also suppress CH_4 emission (*48*). The use of potassium fertilizers reduced CH_4 emission by 49% (*49*). The potassium fertilizer acts similarly to ammonium fertilizers in that it enhances methanothrophs and depresses methanogenic bacteria. These studies suggest optimizing rice yields with ammonium and potassium fertilizers can mitigate CH_4 emission (see Table II for summary of fertilizer and management effects).

Organic Matter Management

The application of organic matter to rice paddies adds available C and often increases CH_4 production (*50*). The application of green manure is a common practice to enhance soil fertilizer and increase long-term N availability. The application of 20 t of *Sesbania rostrata* residues increased CH_4 emission more than three-fold at a field experiment done at the International Rice Research

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Institute (*50*). The application of ammonium fertilizer can reduce the effect of organic amendments on CH_4 emission.

The return of rice straw has also been shown to enhance CH_4 production. The application of 6 to 9 Mg rice straw increased annual CH_4 by 1.8 to 5 fold in studies done in California and Japan (*6*, *35*, *51*). The observed increase in CH_4 emissions is a result of increased available C and changes in the microbial community. The size of the microbial community increases when straw is returned to paddies on a long-term basis (*52*); CH_4 production was positively correlated to the size of the microbial community at different soil temperatures. The return of rice straw is becoming more common for a number of reasons. In developed countries, concerns with air pollution from rice straw burning have prompted returning straw to rice paddies. In tropical countries, the intensification of rice through planting up to three crops annually has increased straw residues loads.

In rainfed systems, wheat grown in the dry season is often rotated with rice grown in the rainy season. Residual wheat straw can also increase CH_4 emission in the following rice crop (*53*). The method of wheat straw incorporation strongly affected CH_4 emission with strip mulching reducing emission by 32 to 42% compared to incorporation or burning.

Rice intensification has been associated with declining rice yields in Asia. It has been proposed that the incomplete decomposition of rice straw under the prolonged flooding regimes in intensified rice has increased inorgnanic N immobilization and hence, decreased N availability (*54*). The fertilizer N has been proposed to bond with the aromatic lignin component of the decomposing rice straw to reduce fertilizer N availability. Therefore, the return of rice straw to paddies could increase future CH_4 emissions from rice and reduce N availability, both of which need to be addressed to determine appropriate management practices for sustainable rice production.

Water Management

Flooded rice is the most productive practice to obtain high rice yields currently. Water management in the form of periodic draining during the season is a proven practice to decrease CH_4 emissions from rice paddies (*55*). In-season draining causes a reduction in the rate of CH_4 production and an increase in the rate of oxidation depending on the length of the drain period (*56*). The timing of the drain also influences the extent of CH_4 reduction with early season draining events having less effect. The most CH_4 reduction can be accomplished with drain events during mid season coinciding with tillering and panicle formation. Multiple drain events during the growing season can reduce CH_4 emission by 9 to 80% (*56*–*58*). The main disadvantage of growing season drain events is a reduction in yield and the onset of nitrification that may lead to losses of N_2O (discussed later).

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Effect of Temperature

Climate variation can have large impacts on annual rice yields. Increases in diurnal air temperature often lead to increased crop biomass assuming no other limiting factors such as water and nutrient availability. In rice, an increase in air temperature often leads to increased vegetative growth, but can negatively impacts grain production (*59*). Spikelet fertility declined from 100% fertile to 10% when temperatures increased from 32 to 40°C (*58*). The absence of a grain sink could increase CH_4 emission through excess allocation of photosynthate to the rhizosphere (*28*).

Changes in daily and diurnal temperatures directly affect CH_4 emission. The direct effect of increasing temperature on CH_4 production, as with most enzymatic processes, is to increase its rate of production (*52*). The diel soil temperature change results in a diurnal pattern of CH_4 emission (*6*, *60*). Methane emission increased in the morning and approached its maximum in the mid-afternoon, coinciding with maximum daily temperature (*60*). In a Mediterranean rice system, maximum CH_4 emission was observed at midnight corresponding to a peak in nighttime plant respiration (*6*). Increased nighttime temperatures due to global warming may change diurnal CH_4 emission patterns.

Elevated CO_2 Effects on Methane Emission

Many elevated CO_2 studies suggest that increasing atmospheric CO_2 will increase rice yield (*61–63*). Increases in root growth and rhizodeposition under elevated CO_2 are routinely reported (*61*, *64*). For these reasons, elevated CO_2 leads to an increase in CH_4 emission from 38 to 60% over ambient CO_2 (*61–63*). Higher photosynthesis potential under elevated CO_2 likely leads to increased rhizodeposition increasing the available C supply for methanogens. Long-term elevated CO_2 exposure in the field was shown to increase CH_4 production in soil incubation studies suggesting a continuous accumulation of available soil C (*63*). The increase in above- and below-ground biomass could only partly explain increased CH_4 emission under elevated CO_2. It was concluded that increased root turnover under elevated CO_2 and temperature in elevated CO_2 experiments was responsible for increased CH_4 emission.

Nitrous Oxide Emissions in Rice

There are considerably fewer studies on N_2O emissions in rice compared to CH_4. Since irrigated rice is the most common system grown throughout the world, deep water and rainfed rice systems will not be considered in this discussion. The emission of N_2O in irrigated systems kept consistently flooded is relatively low compared to CH_4, especially considering the net global warming potential of the total GHGs emitted. Practices of seasonal drain events done to apply pesticides can increase N_2O emission depending on the duration and frequency of the draining periods. A number of factors affect N_2O emission, but the most important is the application of fertilizer N, including fertilizer N type, and use of nitrification inihibitors and slow release fertilizers (Table II). Crops in rotation

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

with rice, commonly wheat, will emit N_2O depending on the amount of residual fertilizer N remaining from either rice and wheat crops or other rotation crops. The foundamental question becomes “Can in-season draining events that mitigate CH_4 emissions reduce the overall global warming potential of GHGs given the probable increase in N_2O emissions?”

Fertilizer N Impacts on Nitrous Oxide Emission

Many studies have shown that fertilizer N inputs, particularly ammonium based N sources, can reduce CH_4 emission (see earlier discussion). A meta analysis of fertilizer usage in rice in China shows an increase in fertilizer applications from 1950 to 1990 of 88 kg N ha^{-1} to 225 kg N ha^{-1}, respectively (*65*). Increasing N addition was shown to increase N_2O emissions 5 to 6 times with N inputs up to 200 kg ha^{-1} and up to 14 times when N inputs were 270 kg N ha^{-1} (*66*) (Figure 4). Higher N_2O emissions were observed in a flood-drain-flood-moist field (F-D-F-M) compared to a flood-drain-flood (F-D-F) field. The moist field period is practiced in China for water savings. Despite only about 1% of the N applied being emitted as N_2O, the increase in fertilizer N applications has significantly increased N_2O emissions over-time (*65*, *67*, *68*). The 1% emission factor (amount of N_2O emitted per unit of fertilizer N added) for N_2O from fertilizer additions is currently used in the most current IPCC assessment for rice cropping systems (*7*). The N_2O emission factor has increased significantly with increasing N additions in rice of up to 400 kg N ha^{-1} (*69*). At typical fertilizer N application rates of 100 to 200 kg N ha^{-1}, N_2O emissions accounted for 0.02 to 0.42% of the applied N (*68*, *69*). The results suggest that the IPCC emission factor is likely overestimating N_2O emissions in rice under typical fertilizer N application rates.

Effect of Flood Management on N_2O Emission

Unfortunately, in-season drain events are the most effective way to reduce CH_4 emissions, but often lead to increased N_2O emissions (*70–73*). In-season drain events quickly reverse anoxic conditions to oxic that begin the nitrification process. The extent of nitrification depends primarily on the duration of the drain event and the amount of fertilizer N not removed by the growing rice crop. Therefore, the timing of the drain events is critical in determining the amount of residual fertilizer ammonium available for nitrification and nitrification-denitrification processes. The duration of the drain event influences the amount of nitrification and therefore NO_3^- available for denitrification when the soil is reflooded. In a Thailand rice study, the emission of N_2O was more related to the number of drain days than the number of drain events (*74*). Fewer total drain days kept the soil more reduced and upon reflooding, anoxic conditions were more quickly reestablished compared to drain events lasting more than a few days. However, in-season drain events, regardless of the duration and frequency, can lead to up to a 10% or greater reduction in rice yield (*74*). In many studies on in-season draining, the amount of N_2O produced can be significant, but if management to reduce the total number of days drained, the total overall warming potential of GHGs emitted is often reduced (*70*, *72*, *74*, *75*).

Organic Matter Application Effects on Nitrous Oxide Emission

The addition of organic matter to rice paddies is done to satisfy soil fertility for both short and long-term rice production. The applications include green manure, rice residue, manure and composted products. Composted materials generally reduce CH_4 emissions as discussed earlier, and have been shown to reduce N_2O emissions (*76*). The application of rice straw often reduces N_2O emission (*66*). Straw with a high C to N ratio likely immobilizes available N reducing its availability for both nitrification and denitrification. Low C to N ratio materials such green manure and legume residues can increase N_2O emission. The addition of high C to N ratio straw decreased N_2O emission by 19% in a Chinese study (*70*). In another study, the application of high C to N rice straw decreased up to 30% compared to no straw addition (*76*). In contrast, the application of rapeseed cake with a low C to N ratio of 8 increased N_2O emissions by 17% (*70*). Long-term application of high C to N rice straw application increases N availability and may increase N_2O emission (*77*).

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

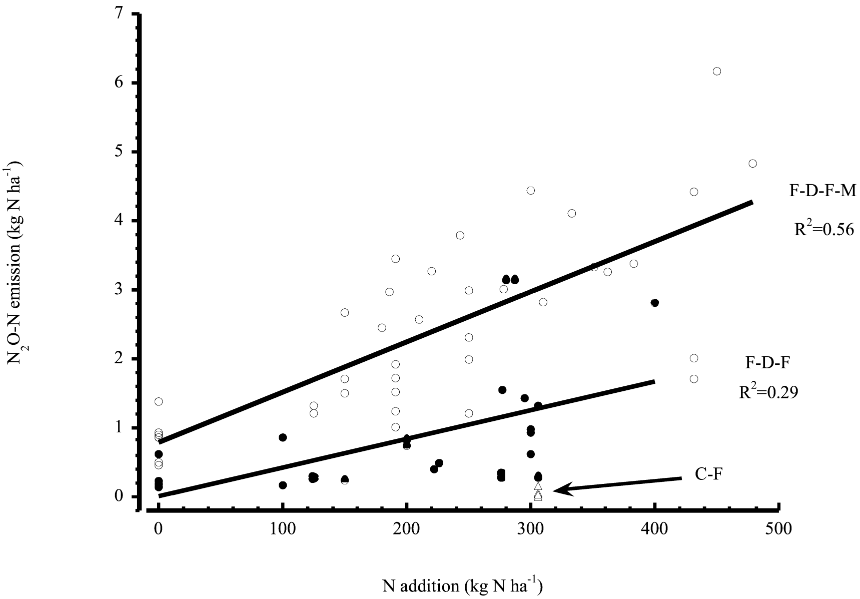


Figure 4. Relationship between fertilizer N applications and nitrous oxide emission in rice. Data graphed from Zou et al. 2007 (68).

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Cultivar Influence on Nitrous Oxide Emission

Similar to CH_4 emission, rice cultivar can influence N_2O emissions. The emission of N_2O has been shown to be emitted through the rice plant, similar to CH_4 (*78*). Though this observation has not been widely confirmed, emitting N_2O through the aerenchyma tissue allows the N_2O to escape to the atmosphere before it has the opportunity to be further reduced in the anoxic zone of the soil. As has been posited for CH_4, lower yielding rice varieties tended to have increased N_2O emissions compared to higher yielding varieties (*79*). The root to shoot ratio and soil NO_3^- content were the most significant factors affecting N_2O emission (*79*). These studies show that optimizing yields and selecting for varieties that reduce N_2O emissions are important in reducing overall GHG emissions in rice.

Nitrification Inhibitors

The use of nitrification inhibitors has been widely shown to reduce N_2O emissions in a wide range of crops (*37*). As shown in Table II, the use of the common nitrification inhibitor dicyandiamide decreased N_2O emission in rice up to 50% (*38*). The use of hydrolysis urease inhibitor hydroquinone reduces the hydrolysis of urea to NH_4^+, the substrate for nitrifiers. On average, urease inhibitors with nitrification inhibitors reduce N_2O emission by 50% (*38*). In practice, hydroquinone and dicyandiamide are often applied together to produce a synergistic effect in reducing the substrate (NH_4^+) and the process of nitrification (*80*). Other methods such as the use of slow release fertilizers are also effective in reducing N_2O emission, but their use in rice has been limited mainly due to the increased cost compared to conventional fertilizer formulations.

Summary

Rice systems are primarily irrigated ephemeral wetlands that emit potent GHGs, primarily CH_4. Rice systems contribute more than 25% of the global anthropogenic CH_4 emissions annually and therefore remain an important source of GHGs. The application of organic matter, especially fresh residues and other low C to N ratio materials that enhance nutrient availability, significantly increases CH_4 emission from rice. Composted organic matter can reduce CH_4 emission compared to fresh or low C to N ratio materials. Rice varieties and cultivars also affect CH_4 emission by conducting variable amounts of CH_4 from the anoxic soil to the atmosphere. There is evidence to suggest that certain rice cultivars and hybrids can reduce CH_4 emission by increasing oxidation potential in the rhizosphere. Increased tillering, through fertilizer N management and plant selection, can increase CH_4 emission by increasing the number of shoots or conduits from the soil to the atmosphere. Mitigating CH_4 emission from rice paddies can be achieved by in-season draining events. Draining just before maximum grain development can lower CH_4 emissions by more than 50%. The use of ammonia based fertilizers has shown a consistent decrease in CH_4 emission compared to organic amendments and nitrate-based fertilizers.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Estimates for global N_2O emissions from rice are lacking but presumed to be low because of the maintenance of anoxic conditions that reduces nitrification. In-season draining of rice paddies is becoming more common to increase the efficacy of pesticides and to mitigate CH_4 emission. The frequency and duration of the drain events directly affect N_2O emission through nitrification. As nitrification is favored by drain management, both nitrifier denitrification and denitrification process can emit N_2O from rice systems. Overall, short duration drain events will likely increase N_2O emission but the reduction in CH_4 emission will likely lower the overall warming potential of the GHGs emitted. The use of nitrification inhibitors can significantly reduce N_2O emissions.

Rice is an important food crop required by a growing human population. The studies presented in this review show the potential to reduce GHG emissions of rice while maintaining production potential required to feed human population growth. Future research will need to address the slowing gains in yield potential to achieve the predicted 50% increase in food supply needed by 2050. It is not likely that rice production area will increase, due to limiting water resources for irrigation. Therefore, rice productivity must be increased on the same or declining land base. Increasing atmospheric CO_2 concentrations has been shown to increase productivity, but unfortunately also CH_4 emissions. Expansion of upland rice will likely occur to compensate for the yield limitations in irrigated rice, but will lead to increased N_2O emissions. As the human population expands, nations will need to weigh the positives and negatives of GHG emissions from agricultural activities. As shown in this review, mitigation of GHGs from rice is achievable without a significant yield penalty, providing an opportunity for agriculture to reduce its total GHG footprint.

References

1. Scheehle, E. A.; Kruger, D. Global anthropogenic methane and nitrous oxide emissions. *Energy J.* **2006**, 33–44.
2. Parry, M. A. J.; Hawkesford, M. J. Food security: increasing yield and improving resource use efficiency. *Proc. Nutr. Soc.* **2010**, *69* (4), 592–600.
3. Horie, T.; Baker, J. T.; Nakagawa, H.; Matsui, T.; Kim, H. Y. Crop ecosystem responses to climatic change: rice. In *Climate Change and Global Crop Productivity*; Reddy, K. R., Hodges, H. F., Eds.; CABI: New York, 2000; pp 81−106.
4. FAO, FAOSTAT. In *Crops*; Food and Agriculture Organization: 2010.
5. Olk, D. C.; Cassman, K. G.; Randall, E. W.; Kinchesh, P.; Sanger, L. J.; Anderson, J. M. Changes in chemical properties of organic matter with intensified rice cropping in tropical lowland soil. *Eur. J. Soil Sci.* **1996**, *47* (3), 293–303.
6. Bossio, D. A.; Horwath, W. R.; Mutters, R. G.; van Kessel, C. Methane pool and flux dynamics in a rice field following straw incorporation. *Soil Biol. Biochem.* **1999**, *31* (9), 1313–1322.
7. Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K. B.; Tignor, M.; Miller, H. L. Contribution of Working Group I to the Fourth

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Assessment Report of the Intergovernmental Panel on Climate Change, 2007. Cambridge University Press: Cambridge, 2007.

8. Dlugokencky, E. J.; Masarie, K. A.; Lang, P. M.; Tans, P. P. Continuing decline in the growth rate of the atmospheric methane burden. *Nature* **1998**, *393*, 447–451.
9. Rigby, M.; Prinn, R. G.; Fraser, P. J.; Simmonds, P. G.; Langenfelds, R. L.; Huang, J.; Cunnold, D. M.; Steele, L. P.; Krummel, P. B.; Weiss, R. F.; O'Doherty, S.; Salameh, P. K.; Wang, H. J.; Harth, C. M.; Muhle, J.; Porter, L. W. Renewed growth of atmospheric methane. *Geophy. Res. Lett.* **2008**, *35* (22).
10. Reeburgh, W. S. Global methane biogeochemistry. In *Treatise on geochemistry:The atmosphere*; Keeling, R. F., Holland, H. D., Turekian, K. K., Eds.; Elsevier-Pergamon: Oxford, UK, 2003; Vol. 4, pp 65−89.
11. Schutz, H.; Seiler, W.; Conrad, R. Processes involved in formation and emission of methane in rice paddies. *Biogeochemistry* **1989**, *7*, 33–53.
12. Conrad, R. Microbial Ecology of Methanogens and Methanotrophs. In *Advances in Agronomy*; Sparks, D. L., Ed.; Elsevier: San Francisco, 2007; Vol. 96, pp 1−64.
13. Conrad, R. Contributions of hydrogen to methane productionand controlof hydrogen concentrations in methanogenic soils and sediments. *FEMS Microbiol. Ecol.* **1999**, *28*, 193–202.
14. Neue, H. Methane emision from rice fields:Wetland rice fields make a major contribution to global warming. *BioScience* **1993**, *43* (7), 466–473.
15. Wrage, N.; Velthof, G. L.; van Beusichem, M. L.; Oenema, O. Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biol. Biochem.* **2001**, *33* (12-13), 1723–1732.
16. Kirk, G. *The Biogeochemistry of Submerged Soils*; John Wiley and Sons Ltd.: West Sussex, 2004; p 291.
17. Horwath, W. R. Carbon Cycling and Formation of Soil Organic Matter. In *Soil Microbiology, Ecology and Biochemistry*; Paul, E. A., Ed.; Academic Press: New York, 2007; pp 303−339.
18. Watanabe, A.; Takeda, T.; Kimura, M. Evaluation of origins of CH_4 carbon emitted from rice paddies. *J. Geophys. Res., [Atmos.]* **1999**, *104* (D19), 23623–23629.
19. Kimura, M.; Murase, J.; Lu, Y. H. Carbon cycling in rice field ecosystems in the context of input, decomposition and translocation of organic materials and the fates of their end products (CO_2 and CH_4). *Soil Biol. Biochem.* **2004**, *36* (9), 1399–1416.
20. Fitzgerald, G. J.; Scow, K. M.; Hill, J. E. Fallow seasonstraw and water management effectson methane emissions in California rice. *Global Biogeochem. Cycles* **2000**, *14* (3), 767–776.
21. Babu, Y. J.; Li, C.; Frolking, S.; Nayak, D. R.; Datta, A.; Adhya, T. K. Modelling of methane emissions from rice-based production systems in India with the denitrification and decomposition model: Field validation and sensitivity analysis. *Curr. Sci.* **2005**, *89* (11), 1904–1912.
22. Fumoto, T.; Kobayashi, K.; Li, C.; Yagi, K.; Hasegawa, T. Revising a process-based biogeochemistry model (DNDC) to simulate methane

emission from rice paddy fields under various residue management and fertilizer regimes. *Global Change Biol.* **2008**, *14* (2), 382–402.

23. Whiting, G. J.; Chanton, J. P. Primary Production Control of Methane Emission from Wetlands. *Nature* **1993**, *364* (6440), 794–795.
24. Huang, Y.; Sass, R. L.; Fisher, F. M. Methane emission from Texas rice paddy soils. 1. Quantitative multi-year dependence of CH_4 emission on soil, cultivar and grain yield. *Global Change Biol.* **1997**, *3* (6), 479–489.
25. Nugroho, S. G.; Sunyoto; Lumbanraja, J.; Suprapto, H.; Ardjasa, W. S.; Kimura, M. Effect of rice variety on methane emission from an Indonesian paddy field. *Soil Sci. Plant Nutr.* **1997**, *43* (4), 799–809.
26. Satpathy, S. N.; Mishra, S.; Adhya, T. K.; Ramakrishnan, B.; Rao, V. R.; Sethunathan, N. Cultivar variation in methane efflux from tropical rice. *Plant Soil* **1998**, *202* (2), 223–229.
27. Corton, T. M.; Bajita, F. S.; Grospe, R. R.; Pamplona, C. A. A.; Wassmann, R.; Lantin, R. S.; Buendia, L. V. Methane emission from irrigated and intensively managed rice fields in Central Luzon (Philippines). *Nutr. Cycling Agroecosyst.* **2000**, *58*, 37–53.
28. van der Gon, H.; Kropff, M. J.; van Breemen, N.; Wassmann, R.; Lantin, R. S.; Aduna, E.; Corton, T. M.; van Laar, H. H. Optimizing grain yields reduces CH_4 emissions from rice paddy fields. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99* (19), 12021–12024.
29. Kludze, H. K.; DeLaune, R. D.; Patrick, W. H. Aerenchyma formation and methane and oxygen exchange in rice. *Soil Sci. Soc. Am. J.* **1993**, *57*, 386–391.
30. Wang, B.; Neue, H. U.; Samonte, H. P. Effect of cultivar difference (’IR72’, ’IR65598’ and ’Dular’) on methane emission. *Agric., Ecosyst. Environ.* **1997**, *62* (1), 31–40.
31. Aulakh, M. S.; Wassmann, R.; Rennenberg, H. Methane transport capacity of twenty-two rice cultivars from five major Asian rice-growing countries. *Agric., Ecosyst. Environ.* **2002**, *91* (1-3), 59–71.
32. Sharkawi, H. M.; Sherif, A.; Zahoor, A.; Faridullah; Yamamoto, S.; Endo, T. Methane emissions and its relation with plant parameters and dissolved oxygen in different rice genotypes. *J. Food, Agri. Env.* **2009**, *7*, 463–470.
33. Kerdchoechuen, O. Methane emission in four rice varieties as related to sugars and organic acids of roots and root exudates and biomass yield. *Agric., Ecosyst. Environ.* **2005**, *108* (2), 155–163.
34. Ma, K.; Qiu, Q. F.; Lu, Y. H. Microbial mechanism for rice variety control on methane emission from rice field soil. *Global Change Biol.* **2010**, *16* (11), 3085–3095.
35. Yagi, K.; Minami, K. Effect of Organic-Matter Application on Methane Emission from Some Japanese Paddy Fields. *Soil Sci. Plant Nutr.* **1990**, *36* (4), 599–610.
36. Wassmann, R.; Neue, H. U.; Bueno, C.; Lantin, R. S.; Alberto, M. C. R.; Buendia, L. V.; Bronson, K.; Papen, H.; Rennenberg, H. Methane production capacities of different rice soils derived from inherent and exogenous substrates. *Plant Soil* **1998**, *203* (2), 227–237.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

37. Akiyama, H.; Yan, X.; Yagi, K. Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N_2O and NO emissions from agricultural soils: meta-analysis. *Global Change Biol.* **2010**, *16*, 1837–1846.
38. Majumdar, D. Methane and nitrous oxide emission from irrigated rice fields: Proposed mitigation strategies. *Curr. Sci.* **2003**, *84* (10), 1317–1326.
39. Yan, X. Y.; Yagi, K.; Akiyama, H.; Akimoto1, H. Statistical analysis of the major variables controlling methane emission from rice fields. *Global Change Biol.* **2005**, *11*, 1131–1141.
40. Wassmann, R.; Lantin, R. S.; Neue, H. U.; Buendia, L. V.; Corton, T. M.; Lu, Y. Characterization of Methane Emissions from Rice Fields in Asia. III. Mitigation Options and Future Research Needs. *Nutr. Cycling Agroecosyst.* **2002**, *58*, 23–36.
41. Watanabe, A.; Kajiwara, M.; Tashiro, T.; Kimura, M. Influence of rice cultivar on methane emission from paddy fields. *Plant Soil* **1995**, *176*, 51–56.
42. Furukawa, Y.; Shiratori, Y.; Inubushi, K. Depression of methane production potential in paddy soils by subsurface drainage systems. *Soil Sci. Plant Nutr.* **2008**, *54*, 950–959.
43. Singh, S. K.; Bharadwaj, V.; Thakur, T. C.; Pachauri, S. P.; Singh, P. P.; Mishra, A. K. Influence of crop establishment methods on methane emission from rice fields. *Curr. Sci.* **2009**, *97* (1), 84–89.
44. Wassmann, R.; Aulakh, M. S.; Lantin, R. S.; Rennenberg, H.; Aduna, J. B. Methane emission patterns from rice fields planted to several rice cultivars for nine seasons. *Nutr. Cycling Agroecosyst.* **2002**, *64* (1-2), 111–124.
45. Ahmad, S.; Li, C. F.; Dai, G. Z.; Zhan, M.; Wang, J. P.; Pan, S. G.; Cao, C. G. Greenhouse gas emission from direct seeding paddy field under different rice tillage systems in central China. *Soil Tillage Res.* **2009**, *106* (1), 54–61.
46. Harada, H.; Kobayashi, H.; Shindo, H. Reduction in greenhouse gas emissions by no-tilling rice cultivation in Hachirogata polder, northern Japan: Life-cycle inventory analysis. *Soil Sci. Plant Nutr.* **2007**, *53* (5), 668–677.
47. Bodelier, P. L. E.; Roslev, P.; Henckel, T.; Frenzel, P. Stimulation by ammonium-based fertilizers of methane oxidation in soil around rice roots. *Nature* **2000**, *403* (6768), 421–424.
48. Kara, E. E.; Ozdilek, H. G. The Effect of Nitrogenous Fertilizers on Methane Oxidation in Soil. *Ekoloji* **2010**, *19* (74), 1–9.
49. Babu, Y. J.; Nayak, D. R.; Adhya, T. K. Potassium application reduces methane emission from a flooded field planted to rice. *Biol. Fertil. Soils* **2006**, *42* (6), 532–541.
50. Vandergon, H.; Neue, H. U. Influence of organic-,atter incoporation on methan emissions from a wetland rice field. *Global Biogeochem. Cycles* **1995**, *9* (1), 11–22.
51. Sass, R. L.; Fisher, F. M.; Lewis, S. T.; Jund, M. F.; Turner, F. T. Methane emissions from rice fields - effect of soil properties. *Global Biogeochem. Cycles* **1994**, *8* (2), 135–140.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

52. Devevre, O. C.; Horwath, W. R. Decomposition of rice straw and microbial carbon use efficiency under different soil temperatures and moistures. *Soil Biol. Biochem.* **2000**, *32*, 1773–1785.
53. Ma, J.; Xu, H.; Yagi, K.; Cai, Z. C. Methane emission from paddy soils as affected by wheat straw returning mode. *Plant Soil* **2008**, *313* (1-2), 167–174.
54. Schmidt-Rohr, K.; Mao, J. D.; Olk, D. C. Nitrogen-bonded aromatics in soil organic matter and their implications for a yield decline in intensive rice cropping. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101* (17), 6351–6354.
55. Sass, R. L.; Fisher, F. M.; Wang, Y. B. Methane emission from rice fields: The effect of floodwater management. *Global Biogeochem. Cycles* **1992**, *6*, 249–262.
56. Sigren, L. K.; Lewis, S. T.; Fisher, F. M.; Sass, R. L. Effects of field drainage on soil parameters related to methane production and emission from rice paddies. *Global Biogeochem. Cycles* **1997**, *11* (2), 151–162.
57. Minamikawa, K.; Sakai, N. The practical use of water management based on soil redox potential for decreasing methane emission from a paddy field in Japan. *Agric., Ecosyst. Environ.* **2006**, *116* (3-4), 181–188.
58. Tyagi, L.; Kumari, B.; Singh, S. N. Water management - A tool for methane mitigation from irrigated paddy fields. *Sci. Total Environ.* **2010**, *408* (5), 1085–1090.
59. Horie, T. Predicting the effects of climate variation and the effect of CO_2 on rice in Japan. *J. Agric. Meteorol.* **1993**, *48*, 567–574.
60. Wang, B.; Neue, H. U.; Samonte, H. P. The effect of controlled soil temperature on diel CH_4 emission variation. *Chemosphere* **1997**, *35* (9), 2083–2092.
61. Ziska, L. H.; Moya, T. B.; Wassmann, R.; Namuco, O. S.; Lantin, R. S.; Aduna, J. B.; Abao, E.; Bronson, K. F.; Neue, H. U.; Olszyk, D. Long-term growth at elevated carbon dioxide stimulates methane emission in tropical paddy rice. *Global Change Biol.* **1998**, *4* (6), 657–665.
62. Cheng, W. G.; Sakai, H.; Hartley, A.; Yagi, K.; Hasegawa, T. Increased night temperature reduces the stimulatory effect of elevated carbon dioxide concentration on methane emission from rice paddy soil. *Global Change Biol.* **2008**, *14* (3), 644–656.
63. Lou, Y. S.; Mizuno, T.; Kobayashi, K.; Okada, M.; Hasegawa, T.; Hoque, M. M.; Inubushi, K. CH_4 production potential in a paddy soil exposed to atmospheric CO_2 enrichment. *Soil Sci. Plant Nutr.* **2006**, *52* (6), 769–773.
64. Inubushi, K.; Cheng, W. G.; Aonuma, S.; Hoque, M. M.; Kobayashi, K.; Miura, S.; Kim, H. Y.; Okada, M. Effects of free-air CO_2 enrichment (FACE) on CH_4 emission from a rice paddy field. *Global Change Biol.* **2003**, *9* (10), 1458–1464.
65. Zou, J. W.; Huang, Y.; Qin, Y. M.; Liu, S. W.; Shen, Q. R.; Pan, G. X.; Lu, Y. Y.; Liu, Q. H. Changes in fertilizer-induced direct N_2O emissions from paddy fields during rice-growing season in China between 1950s and 1990s. *Global Change Biol.* **2009**, *15* (1), 229–242.
66. Ma, J.; Li, X. L.; Xu, H.; Han, Y.; Cai, Z. C.; Yagi, K. Effects of nitrogen fertiliser and wheat straw application on CH_4 and N_2O emissions from a paddy rice field. *Aust. J. Soil Res.* **2007**, *45* (5), 359–367.

67. Denmead, O. T.; Freney, J. R.; Simpson, J. R. Nitrous oxide emission during denitrofication in a flooded field. *Soil Sci. Soc. Am. J.* **1979**, *43* (4), 716–718.
68. Mosier, A. R.; Chapman, S. L.; Freney, J. R. Determination of dinitrogen emission and retention in floodwater and porewater of a lowland rice field fertilized with N-15-urea. *Fertil. Res.* **1989**, *19* (3), 127–136.
69. Zou, J. W.; Huang, Y.; Zheng, X. H.; Wang, Y. S. Quantifying direct N_2O emissions in paddy fields during rice growing season in mainland China: Dependence on water regime. *Atmos. Environ.* **2007**, *41* (37), 8030–8042.
70. Zou, J. W.; Huang, Y.; Jiang, J. Y.; Zheng, X. H.; Sass, R. L. A 3-year field measurement of methane and nitrous oxide emissions from rice paddies in China: Effects of water regime, crop residue, and fertilizer application. *Global Biogeochem. Cycles* **2005**, *19* (2).
71. Yue, J.; Shi, Y.; Liang, W.; Wu, J.; Wang, C. R.; Huang, G. H. Methane and nitrous oxide emissions from rice field and related microorganism in black soil, northeastern China. *Nutr. Cycling Agroecosyst.* **2005**, *73* (2-3), 293–301.
72. Jiang, C. S.; Wang, Y. S.; Zheng, X. H.; Zhu, B.; Huang, Y.; Hao, Q. J. Methane and nitrous oxide emissions from three paddy rice based cultivation systems in southwest China. *Adv. Atmos. Sci.* **2006**, *23* (3), 415–424.
73. Li, X. L.; Zhang, X. Y.; Xu, H.; Cai, Z. C.; Yagi, K. Methane and nitrous oxide emissions from rice paddy soil as influenced by timing of application of hydroquinone and dicyandiamide. *Nutr. Cycling Agroecosyst.* **2009**, *85* (1), 31–40.
74. Towprayoon, S.; Smakgahn, K.; Poonkaew, S. Mitigation of methane and nitrous oxide emissions from drained irrigated rice fields. *Chemosphere* **2005**, *59* (11), 1547–1556.
75. Abao, E. B.; Bronson, K. F.; Wassmann, R.; Singh, U. Simultaneous records of methane and nitrous oxide emissions in rice-based cropping systems under rainfed conditions. *Nutr. Cycling Agroecosyst.* **2000**, *58*, 131–139.
76. Yao, Z. S.; Zhou, Z. X.; Zheng, X. H.; Xie, B. H.; Mei, B. L.; Wang, R.; Butterbach-Bahl, K.; Zhu, J. G. Effects of organic matter incorporation on nitrous oxide emissions from rice-wheat rotation ecosystems in China. *Plant Soil* **2010**, *327* (1-2), 315–330.
77. Eagle, A. J.; Bird, J. A.; Horwath, W. R.; Linquist, B. A.; Brouder, S. M.; van Kessel, C. Rice yield and nitrogen utilization efficiency under alternative straw management practices. *Agron. J.* **2000**, *92*, 1096–1103.
78. Mosier, A. R.; Mohanty, S. K.; Bhadrachalam, A.; Chakravorti, S. P. Evoluation of dinitrogen and nitrous oxide from the soil to the atmosphere through rice plants. *Biol. Fertil. Soils* **1990**, *9* (1), 61–67.
79. Baruah, K. K.; Gogoi, B.; Gogoi, P.; Gupta, P. K. N_2O emission in relation to plant and soil properties and yield of rice varieties. *Agron. Sustainable Dev.* **2010**, *30* (4), 733–742.
80. Li, X. L.; Zhang, G. B.; Xu, H.; Cai, Z. C.; Yagi, K. Effect of timing of joint application of hydroquinone and dicyandiamide on nitrous oxide emission from irrigated lowland rice paddy field. *Chemosphere* **2009**, *75* (10), 1417–1422.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch005

Chapter 6

Understanding Greenhouse Gas Emissions from Croplands in China

Zucong Cai* **and Xiaoyuan Yan**

State Key Laboratory of Soil and Sustainable Agriculture,
Institute of Soil Science, Chinese Academy of Sciences,
Nanjing 210008, China
***E-mail: zccai@issas.ac.cn**

China is the most important crop producing country, accounting for about 30% of total rice production and total N-fertilizer consumption worldwide. Due to the physiological demands of the rice plant, flooded conditions are required at certain growth stages. An anaerobic fermentative product, methane (CH_4), is produced and emitted in the rice fields under flooded conditions. There are very large temporal and spatial variations of CH_4 emissions from rice fields in China, with seasonal average fluxes in the range 0.14–58 mg CH_4 m^{-2} h^{-1}, mainly dependent on water regime in both off-rice and rice seasons, and availability of labile organic carbon. Based on field measurements, recent estimates of CH_4 emission from Chinese paddy fields, either by modeling or by scaling up, were mostly in the range 3.3–9.6 Tg CH_4 y^{-1}, with a more realistic value of around 8 Tg CH_4 y^{-1}. Seasonal nitrous oxide (N_2O) emission varied greatly, from near zero to > 12 kg N_2O-N ha^{-1} for upland crops and rice. Field measurements revealed that rice fields are also an important N_2O source, but that fertilizer-induced N_2O emission factor is lower than that for upland crops, ranging from near zero to 0.7%, dependent on water regime. Mainly based on the soil dataset from the Second National Soil Survey conducted during 1979–1982, a number of studies quantified the soil organic carbon (SOC) pool in China and showed that SOC was in the range of 85–95 Pg in the top 100 cm. Mainly due to continuous increases in crop yield, the area of conservation tillage, and the return of crop residues to croplands, SOC increased at 13–28

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Tg y^{-1} in the surface layer of Chinese croplands during the last three decades. There is a large potential for mitigating CH_4 and N_2O emissions from croplands and sequestering organic carbon in cropland soils by improving water regimes and nitrogen use efficiency for both upland crops and rice, appropriate management of crop residues, and reduced tillage in semi-arid regions. Meanwhile, the synergies and trade-off relationships between greenhouse gas emissions should be taken fully into account for any options pursued.

1. Introduction

China is one of the largest crop-producing countries, although the area of cropland varies greatly according to various data sources. The total area of croplands in China was 121.72 Mha in 2008. Rice is the most important food crop, followed by maize and wheat. The rice harvested area increased steadily from 27 Mha in 1961 to 36.97 Mha in 1976, decreased continuously to 26.78 Mha in 2003, and then increased again slowly to around 29.93 Mha in 2009. In contrast with the great fluctuation in rice, the maize harvested area increased steadily from around 15 Mha in 1961 to around 30 Mha in 2009. Similarly to the rice harvested area, the wheat harvested area increased from 1961 to the early 1990s, decreased until 2003, and then slowly increased. It is noteworthy that the harvested area of vegetables increased dramatically after 1961, reaching 9 Mha in 2009 (Figure 1).

There is a significant spatial variation of cropping systems from south to north China. For the staple crops, south China is dominated by rice cultivation, including double rice cultivation (i.e. early rice followed by late rice in the same year) and single rice cultivation. North China is dominated by summer maize and winter wheat. However, since the late 1970s, the rice harvested area has reduced continuously in south China and expanded in northeast China. In Heilongjiang Province, the most northeast province, the rice harvested area increased from 0.21 Mha in 1980 to 2.25 Mha in 2007 (i.e. by ten times). In contrast, in the same period, the rice harvested area decreased from 4.16 to 1.94 Mha in the southern province of Guangdong (*2*).

Croplands of China are characterized by intensive use, as indicated by high multiple cropping indices and large inputs of chemicals, including fertilizers, pesticides and herbicides. The national average cropping index was 142% at the end of the 1990s (*3*). The cropping system of double rice crop followed by winter crops such as oil seed rape used to prevail in southern China. Summer maize and winter wheat, two crops per year, is the prevailing cropping system of north China. China's consumption of chemical fertilizers increased from 0.72×10^6 t in 1961 to 15.33×10^6 t in 1980, and to 47.66×10^6 t in 2005 (*1*). China now consumes about one third of the total nitrogen (N) fertilizers in the world.

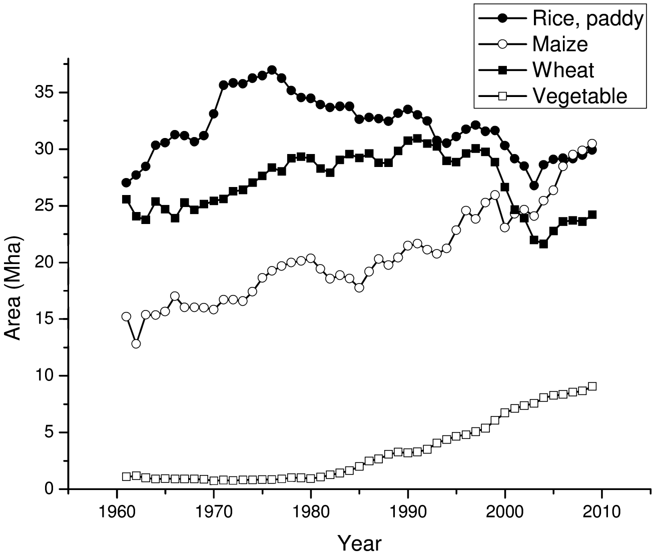


Figure 1. Temporal variation in harvested areas of rice, wheat, maize and fresh vegetables in China during 1961–2009 (1).

The research on greenhouse gas emissions from croplands started in China in the late 1980s and the first paper on methane (CH_4) and N gases emissions from Chinese cropland was published in 1988 (*4*). Since CH_4 fluxes measured in a rice field in Tuzu, Sichuan Province of China were, on average, 60 mg m^{-2} h^{-1} (i.e. 4–10 times higher than emission rates from rice fields in the United States and Europe (*5*)), great attention was drawn to measurement and understanding of CH_4 emissions from rice fields in China. The first paper reporting N_2O emissions from croplands in China was Wang et al. (*6*). Up to the present, CH_4 and N_2O emissions from croplands in China have been intensively measured, the factors affecting their emissions investigated, and the annual emissions at the national and regional scales have been estimated by various approaches. The storage of soil organic carbon (SOC) and changes in croplands were also estimated by various approaches. Almost all research on SOC has used the dataset resulting from the Second National Soil Survey (conducted during the late 1970s to the early 1980s) to estimate the baseline SOC content or storage. Although there are still uncertainties, the estimated CH_4 and N_2O emissions from croplands, and storage and changes in SOC in cropland soils have been estimated within relatively narrow ranges.

2. CH_4 Emissions from Rice Fields

Since the first report on CH_4 emission from Chinese rice fields, a great number of studies have been conducted on this issue, including field measurements, analysis of influencing factors, searching for mitigation options, and estimation of emission at various scales.

2.1. Factors Influencing CH_4 Emissions from Rice Fields

CH_4 emission from rice fields is the net result of three processes: production, oxidation and transport. Any factors that affect one or more of these processes may affect CH_4 emission. By analyzing field measurement data of CH_4 emission from rice paddies in Asia, Yan et al. (*7*) found that organic amendment, water regime during the rice-growing season, water status in pre-season and soil properties were the main influencing factors.

2.1.1. Organic Amendments

CH_4 is converted from substrate by methanogenic bacteria in strictly reduced environments. Organic amendments directly supply substrate for methanogenic bacteria. The decomposition of organic materials also helps develop a reduced environment for CH_4 generation. CH_4 emission from rice paddies is affected by the type, amount and timing of organic amendment.

A variety of organic fertilizers are used in China, including crop residues, green manure, animal manure, and compost from biogas reactors. The stimulating effect of all these organic fertilizers on CH_4 emission from Chinese rice paddies has been widely studied (*8–12*). Yan et al. (*13*) compiled 15 pairs of flux data, comparing CH_4 emissions from Chinese rice fields with and without organic amendment, controlling for other conditions (i.e. site, rice season and water regime). The ratios of CH_4 flux with organic amendment to flux without organic amendment were within the range 0.7–4.2, with an average of 2.08 and standard deviation of 1.16. However, there is a large difference in the effects of different types of organic materials on CH_4 emission. Generally, fresh crop straw shows the largest stimulating effect on CH_4 emission. A seasonal average CH_4 flux of 51.4 mg m^{-2} h^{-1} was reported for rice straw incorporation of 2.63 t ha^{-1}, compared to 10.3 mg m^{-2} h^{-1} without organic input (*11*). Decomposed manure from biogas reactors showed little stimulating effect (Tao et al., 1994). CH_4 emission induced from surface-applied organic materials was less than that from organic materials incorporated into soils, as the former had more chance to be decomposed aerobically than the latter (*14*).

To prevent air pollution and increase soil fertility, the Chinese government banned field burning and encouraged field application of crop residues. This practice is likely to increase CH_4 emission from rice fields. To mitigate the straw-induced CH_4 emission, Ma et al. (*15*) suggested that straw be piled in ridges between rice rows, high above the water layer and be covered with soil.

CH_4 emission could be reduced by one third through this practice as compared with direct incorporation of straw into surface soil.

2.1.2. Water Management during the Rice-Growing Season

The water management practice during the rice-growing season is a critical factor influencing CH_4 emission. Mid-season drainage is widely practiced in Chinese rice cultivation. Yan et al. (*13*) compiled 11 pairs of data that compared the effects of mid-season drainage and continuous flooding on CH_4 emission from Chinese rice fields, controlling for other conditions (i.e. organic input, rice season and site). On average, CH_4 flux from fields with mid-season drainage was 53% of that from continuously flooded fields. During mid-season drainage, the soil is exposed to air and the redox potential increases rapidly, which inhibits the activity of methanogenic bacteria and so lowers CH_4 production (*16*). The increase in soil redox potential also helps the oxidation of CH_4 (*17*). CH_4 emission may gradually resume when mid-season drainage ends and the rice field is re-flooded. However, if the mid-season drainage was performed until the soils becomes very dry, CH_4 emission may not resume even after an extended period of re-flooding, resulting in a greatly reduced seasonal CH_4 emission (*16*). The earlier the mid-season drainage is started, the greater is the mitigation effect (*18*). However, if the mid-season drainage is performed too early, it damages rice growth.

It is worth noting that when drainage begins, the CH_4 trapped in soil may erupt, resulting in a short-term emission peak, which may be overlooked by observers (*16*).

2.1.3. Water Status in Preseason

In addition to water management, the water status of rice fields before the rice-growing season also has a strong influence on CH_4 emission in the rice-growing season. Extremely high CH_4 emission was found for rice fields flooded in the winter season (*19*). For four sites across south and southwest China, Kang et al. found that CH_4 fluxes in the rice-growing season from fields that had been flooded in the preceding winter season were 1.2–6.4 times those from fields that were drained in the preceding winter season (*20*).

If the soil is drained in the preseason, ions such as ammonium (NH_4^+), manganese (Mn^{2+}) and iron (Fe^{2+}) are oxidized. When the soil is flooded for rice-growing, the oxidized ions are gradually reduced, and it takes a long time for the methanogenic organisms to revive, therefore shortening the CH_4 emission period.

There are generally three rice crops in China: single, early and late rice. Single rice is planted on rice fields that are left fallow or planted with upland crops in the preceding season with the fields drained. Early rice is similar to single rice, but the preceding season is shorter. Late rice is usually planted immediately after early rice on the same field. Because the field is usually flooded or kept in moisture conditions suitable for CH_4 production before late rice transplanting, CH_4 fluxes increase sharply soon after transplanting; however, it takes a longer time for CH_4 emission to resume for early rice or single rice (*13*). Due to this difference in water status in preseason, the average CH_4 emission in late rice is 1.5 and 2.3 times that in early rice and single rice, respectively (*13*). CH_4 emission from rice fields can be dramatically reduced when rice is planted after two consecutive upland crops as compared to the cases where rice is alternated with upland crops or rice is continuously cropped (*21*).

2.1.4. Chemical Fertilizer

Application of chemical fertilizer, especially synthetic N, is necessary in Chinese rice cultivation. The effect of N-fertilizer on CH_4 emission from rice paddies has been studied in many field experiments and the results are mixed. Chen et al.found that the application of urea increased CH_4 emission, as urea increased root growth and root exudates, providing more substrate for methanogenesis (*22*). Another effect of urea application is that NH_4^+, the product of urea hydrolysis, inhibits CH_4 oxidation through competition for methanotrophs and thus increases CH_4 emission. Other studies, however, showed that the use of urea decreased CH_4 emission (*12*, *23*, *24*). It was argued that in an environment of high CH_4 concentration, NH_4^+-based N-fertilizer may inhibit CH_4 oxidation at the beginning, but the coexistence of high CH_4 concentration and NH_4^+ stimulates the growth of methanotrophs and/or their activity for oxidizing CH_4. With the gradual NH_4^+ uptake by rice plants, the increased methanotroph population and/or their activity may consume more CH_4, leading to lower CH_4 emission in later stages (*23*).

Compared to urea, the use of ammonium sulfate, $(NH_4)_2SO_4$, consistently decreased CH_4 emission from rice paddies in all studies that compared the effects of the two fertilizers (*8*, *23*, *25*). This was likely due to the inhibitory effect of SO_4^{2-} on methanogenesis.

2.2. Temporal and Spatial Variations of CH_4 Emissions from Rice Fields

Observation of the diurnal variation of CH_4 flux is important to determine the timing of routine monitoring. The majority of such studies in China have shown that the diurnal variation of CH_4 fluxes follows that of surface soil temperature, with peak flux during 14:00–18:00 h (*26*, *27*). This diurnal pattern was attributed to the temperature dependence of CH_4 production and transport. The high temperature in the afternoon stimulates the decomposition of organic materials and evapotranspiration, the former provides substrate for methanogenic bacteria and the latter aids the transport of CH_4 from soil to atmosphere. The diurnal variation can be irregular or random on cloudy and rainy days. The range of diurnal variation of CH_4 fluxes is usually larger in the early stage of rice growth than in later stages. However, Shuangguan et al. argued that too high a temperature in the afternoon may result in the closure of rice stomata and the inhibition of CH_4 transport, while at night, the rice stomata open again and the entrapped CH_4 may be emitted during this period, leading to peak emissions at night (*28*).

The seasonal pattern of CH_4 fluxes is very sensitive to water management in the rice-growing season and the preceding season. A complete mid-season drainage may dramatically reduce CH_4 flux to zero and it takes a long time for this flux to resume. Yan et al. derived general seasonal patterns for early, late and single rice in China. The average flux for early rice in the first 15 d was approximately 0.6 times the seasonal average; subsequently, the moving average was relatively constant, close to the seasonal average (*13*). The late rice flux peaked shortly after rice transplanting; the average flux in the first 15 d was about twice the seasonal average. After this period, the flux decreased rapidly; in the late stage, the flux dropped close to zero. For single rice, the flux increased gradually after transplanting, peaked about 50 d later, and then gradually decreased until the end of the season. These characteristics of general flux patterns are associated with agricultural practices both in the rice season and the preceding season.

There is large variability in CH_4 flux from rice paddies at field, regional and national scales. Cai et al. measured CH_4 fluxes from three similarly managed rice fields located at the bottom, middle and top of a small hilly slope in Jiangxi Province, and found that the seasonal CH_4 flux from the field at the bottom could be as high as four times that from the field at the top. The large difference in CH_4 fluxes was attributed to the soil water status. For fields at the bottom, it was difficult to be completely drained both in the rice-growing and in the preceding season (*29*).

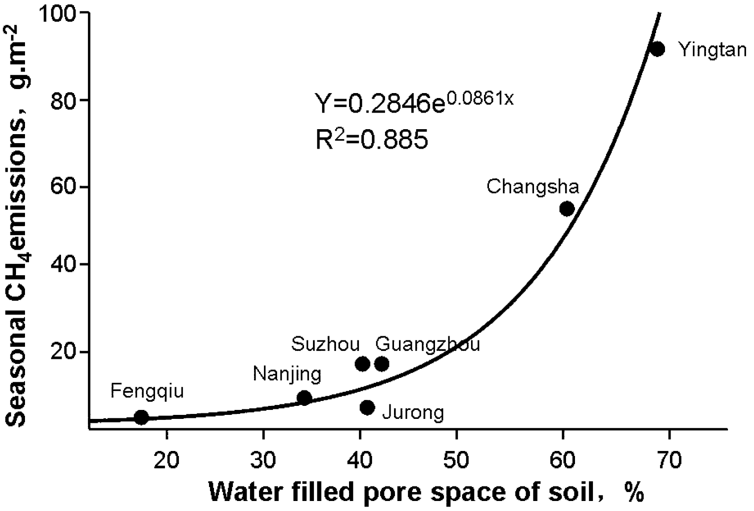


Figure 2. Variation in CH_4 fluxes from rice fields across China and the relationship between seasonal CH_4 emissions and water-filled pore space of soils in the winter season before rice growing.

Our group has measured CH_4 emission from rice paddies in Guangzhou of Guangdong Province, Changsha of Hunan Province, Yingtan of Jiangxi Province, Fengqiu of Henan Province, and Suzhou, Nanjing and Jurong of Jiangsu Province since 1992. In each site, there have been multi-year, multi-treatment measurements. The average seasonal emissions varied from 1.9 g CH_4 m^{-2} in Fengqiu to 90.7 g CH_4 m^{-2} in Yingtan. Although the large spatial variability was partially caused by treatment differences, it was better explained by soil water content in the season preceding rice (Figure 2).

2.3. Estimation of CH_4 Emissions from Rice Fields

As the largest rice producer in the world, China's rice fields have been of particular concern in the past three decades as a source of CH_4, and various estimations have been made (Figure 3). One of the earliest calculations was made by extrapolating a flux of 58 mg CH_4 m^{-2} h^{-1}, the average CH_4 emission flux for the rice-growing season of two consecutive years in Tuzu, Sichuan Province, to the whole of China. The resulting estimate was 30 Tg CH_4 y^{-1} (*5*). Similarly, Wassmann et al. extrapolated the results of measurements in Hangzhou, Zhejiang Province to the entire country, and estimated an emission of 18–28 Tg CH_4 y^{-1} (*30*). As field measurements accumulated, more flux data were included in upscaling methods. Yao et al. used flux data from six sites to represent 10 agroecological zones, and estimated 15.3 Tg CH_4 y^{-1} (*31*). Evaluating results from 12 field sites, Cai concluded that emission was 8.05 Tg CH_4 y^{-1}, and considered the effects of water regime and organic fertilizer application (*32*). With a total of 204 season-treatment measurements conducted on 23 sites, and considering the effect of water regime and organic amendment, Yan et al. estimated an emission of 7.67 Tg CH_4 y^{-1} (*13*).

Several process-based models of various levels of complexity have been developed to estimate CH_4 emission from rice fields in China. Cao et al. developed a simplified process-based CH_4 emission model. Taking rice primary production and soil organic degradation as supplies of carbon (C) substrate for methanogens, and considering environmental controls of methanogenesis, they estimated a total emission of 16.2 Tg y^{-1} for China (*33*). Huang et al. considered daily CH_4 emission flux as a function of photosynthetic activity, and incorporated the effects of organic matter, soil sand content, temperature and rice cultivar, and estimated the emission to be 9.66 Tg CH_4 y^{-1} (*34*). Based on a rice crop simulation model and integrating the effects of climate, soil, agricultural management and the growing of rice on CH_4 flux, Matthews et al. calculated an emission of 3.35–8.64 Tg CH_4 y^{-1} for China, and concluded that a more realistic estimate was 7.22–8.64 Tg CH_4 y^{-1} (*35*).

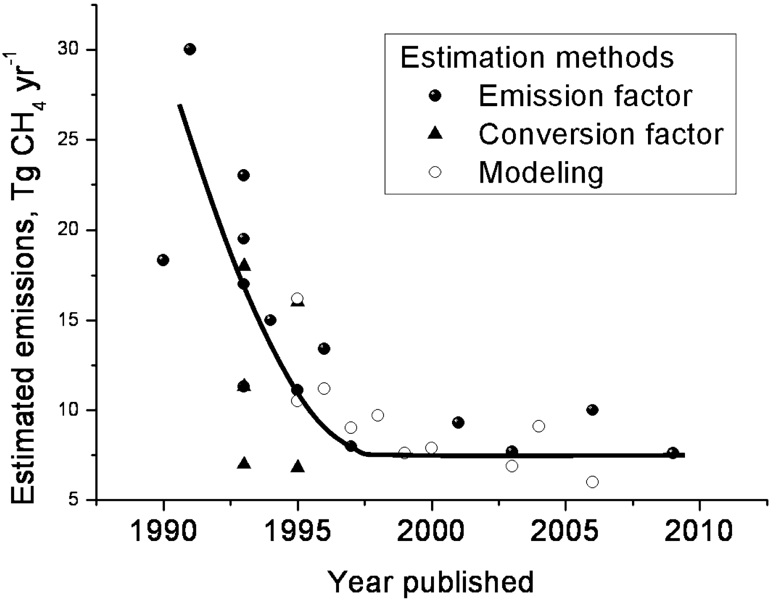


Figure 3. Various estimations of CH_4 emission from Chinese rice fields, obtained by different methods, and published in different years. Figure was drawn with data from Cai et al. (37).

Recently, we applied the tier 1 method of the 2006 IPCC (Intergovermental Panel on Climate Change) guidelines to estimate CH_4 emission from global rice fields – giving global total emission of 25.6 Tg y^{-1}, of which 7.6 Tg was estimated to be emitted from Chinese rice fields (*36*). We have compiled the most up-to-date dataset of CH_4 emissions from Chinese rice fields, with a total of 336 season-treatment measurements; the average of these seasonal measurements was 25.6 g m^{-2}. Simply multiplying this average flux by the total rice cultivation area of about 30 Mha, gives an estimate of 7.68 Tg CH_4 y^{-1}. Considering all the recent estimations obtained with different methods (Figure 3), we are confident that CH_4 emission from Chinese rice fields is around 8 Tg y^{-1}.

3. Nitrous Oxide Emissions from Croplands

Nitrous oxide (N_2O) is an intermediate product of nitrification and denitrification. Its emission is controlled by the availability of substrates and environmental factors. Emission of N_2O has been widely measured for various croplands in China since the 1990s.

3.1. Factors Influencing N_2O Emissions from Croplands

3.1.1. Cropping Systems

Rice is an important crop in China and during most of a rice-growing season, the rice field is flooded. In a flooded environment, nitrification is weak and denitrification proceeds to the end step with N_2 as the dominant product. Therefore N_2O emission from rice paddies was considered negligible in early studies (*38*). However, observations in China showed that although N_2O flux from rice paddies was lower than that for upland crops, a significant amount of N_2O can be emitted from rice paddies, especially after mid-season drainage (e.g. (*23*)). Based on the many field measurements conducted in China and other Asian countries, the IPCC 2006 Guidelines used separate emission factors to estimate N_2O emissions from rice paddies and uplands (*39*)

Yu et al. observed much higher N_2O emission from a soybean field than from a wheat or spinach field (*40*), but their field experiment was not designed for these comparisons. In a pot experiment, Yang and Cai showed that the process of symbiotic N-fixation *per se* did not stimulate N_2O production or emission, but rather senescence and decomposition of roots and nodules in the late growth stage did (*41*).

3.1.2. N Fertilizers

As substrates for nitrification and denitrification, mineral N [i.e. NH_4^+ and nitrate (NO_3^-)] increases N_2O emission. China is the largest N-fertilizer consumer in the world, and many field experiments have been conducted to measured N_2O emission from N-fertilized fields. However, only a limited number of these experiments have included treatments with more than two fertilization rates at comparable conditions enabling a response curve of N_2O emission to fertilizer dose to be drawn. We abstracted the N_2O flux data from this limited number of experiments (Figure 4) – the response of N_2O emission to N dose appears very complex. The flux may increase linearly, exponentially, logarithmically or even decrease with N doses.

Most of the chemical N-fertilizer in China is applied as urea, but few studies have compared the effects of different N-fertilizers on N_2O emission. For an upland soil cropped with summer maize, Xiang et al. found that when applied at the same rate, urea generated more N_2O than $(NH_4)_2SO_4$, which in turn generated significantly higher N_2O emission than KNO_3 (*42*). However, on a rice paddy field, Cai et al. observed higher N_2O emissions from plots supplied with $(NH_4)_2SO_4$ compared to urea (*23*). It is reasonable that NH_4^+-based fertilizer produces more N_2O than NO_3^--based fertilizer since the former undergoes nitrification before denitrification. The comparative effects of urea and $(NH_4)_2SO_4$ on upland and paddy fields were not consistent in the preceding two studies; however, in neither study were the differences statistically significant.

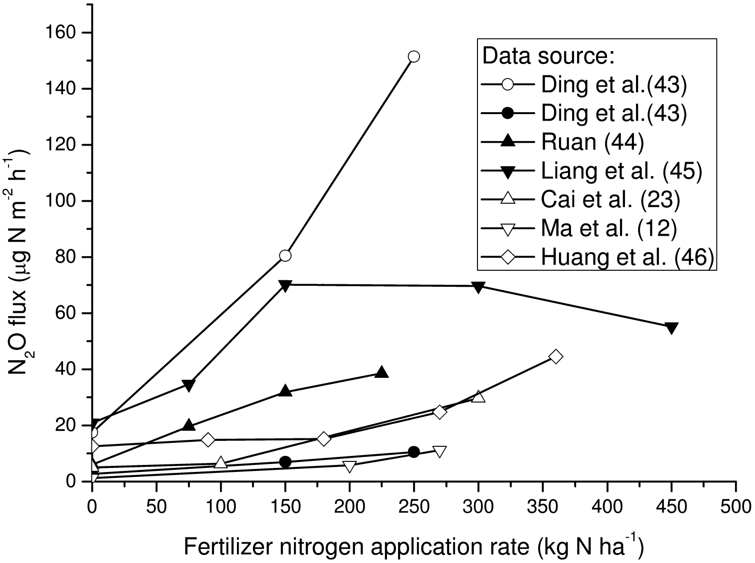


Figure 4. Response of N_2O emissions to fertilizer N application rates observed in Chinese croplands. Data were extracted from references (12, 23, 43–46), as indicated on figure.

3.1.3. Soil Moisture and Changes

Soil moisture is a critical controlling factor for N_2O emission from soils since it affects activity of nitrifiers and denitrifiers, the ratio of N_2O as a product of nitrification and denitrification, and the transport of gases. In a field with a rice–wheat rotation in southeast China, Zheng et al. found that the N_2O emission flux from either fertilized or unfertilized plots increased abruptly with soil moisture at about 105% soil water holding capacity (SWHC), reached a maximum at about 110% SWHC and then quickly decreased to near the baseline at about 115% SWHC (*47*). They reported optimum soil moisture of 110% SWHC for N_2O emission, which was 99% water-filled pore space (WFPS) for that soil. However, in a field with a rice–rape rotation in central China, Lin et al. observed optimum soil moisture content of 75% WFPS (*48*). This difference in optima was probably due to the difference in soil properties, especially soil texture. The soil of Zheng et al. was loam clay and that of Lin et al. was clayey.

Due to the existence of an optimum soil moisture, a wet–dry cycle in rice paddy or rainfall on upland can cause a peak emission of N_2O (*47*, *49*). Yan et al. found that the majority of N_2O emission during the rice-growing season was during mid-season drainage and the beginning of re-flooding (*49*). Paddy rice cultivation in unsaturated soils covered with mulch or plastic film generated extremely high N_2O emission as the soil was kept moist, while N_2O emission from continuously flooded rice was very low (*50*). A tradeoff relationship between CH_4 and N_2O

emissions from rice paddies is frequently observed, mainly due to the effect of soil moisture on their production (e.g. (*23*, *51*)).

3.1.4. Soil Properties

Various soil properties affect N_2O emission from soils. Soil texture may affect oxygen availability, gas diffusion and soil moisture status. On the one hand, fine-textured soils have more capillary pores within aggregates holding water more tightly than do coarse-textured soils and are more prone to N_2O production by either microbial nitrification or denitrification (e.g. (*51*)). On the other hand, fine-textured soils may impede N_2O diffusion and so N_2O has more chance to be denitrified to N_2. As a result, relatively high N_2O emission may occur in loamy soils, because the texture is favorable to both N_2O production and diffusion (*52*).

Generally, SOC favors microbiological activity. Statistical analysis of a large number of field measurement results under various conditions worldwide, showed that N_2O emission increased with SOC content (*53*). In contrast, Huang et al. conducted a pot experiment with a total of 18 fertilized paddy soils collected from Jiangsu Province, China and planted with wheat, and found a clear negative exponential relationship between N_2O emission and SOC content. Another statistical analysis with data only from Asia also found a negative relationship between N_2O emission and SOC content (*54*). It is not clear why N_2O emission decreases with SOC. Huang et al. argued that high SOC content may favor the reduction of N_2O to N_2 (*55*). Due to the tight coupling of SOC and soil N, Huang et al. found a negative relationship between N_2O emission and total soil N content (TN).

Soil pH is one of the strongest influences on N_2O emission as it affects the three most important processes that generate N_2O: nitrification, denitrification and dissimilatory NO_3^- reduction to NH_4^+ (DNRA). Nitrification is often considered to be sensitive to acidity, and optimum values in the range pH 6.5–8.0 have been reported. High pH favors NO_2^- accumulation and the DNRA process. During denitrification the mole fraction of N_2O decreases as pH increases. Therefore, in incubation, a maximum flux of N_2O occurred at pH 6.5 (*56*). The pot experiment of Huang et al., however, showed that N_2O emission increased with soil pH in the range of 5.6–8.6 (*55*). This simple correlation may not reflect the real effect of soil pH on N_2O emission as the effects of other soil properties such as SOC were not excluded. The two statistical analyses that integrated the effects of management and soil properties on N_2O emission indicated an optimum soil pH of 6.5–7.5 (*53*, *54*).

3.2. Temporal and Spatial Variations of N_2O Emissions from Croplands

As N_2O production is very sensitive to N availability and soil moisture, its emission is often sporadic. Clear diurnal variation can only be observed when soil moisture is stable, the soil is not recently fertilized, and the weather is fine. In such cases, the diurnal pattern of N_2O emission follows that of temperature, with peak emission usually during 13:00–17:00 h, and low emissions at night (*51*).

The seasonal pattern of N_2O emission from both upland and rice paddies is basically determined by fertilizer and water management. In a typical seasonal pattern of N_2O emission from a rice paddy (Figure 5) there was almost no N_2O emission during the continuous flooded period before mid-season drainage, even after incorporation of basal fertilizer in soil. With the start of mid-season drainage, N_2O flux increased sharply and peaked three days after commencing mid-season drainage. The flux decreased when the soil became too dry, but increased again when the soil was re-flooded. There were small emission peaks after surface application of topdressing fertilizer and the start of end-season drainage. For N_2O emission from upland or rice paddy fields in an upland crop season, relatively high fluxes occur after fertilization, irrigation and rainfall events (e.g. (*47*, *52*)).

There is large variation in observed seasonal N_2O emissions in China, ranging from near zero to > 12 kg N ha^{-1}. However, soil N_2O emission comprises two components: background and fertilizer-induced emissions. Both components, especially fertilizer-induced N_2O emission, are critically affected by management practices such as irrigation and fertilization. A clear spatial pattern in N_2O fluxes is therefore not expected. However, Gu et al. estimated the background emissions from croplands in China at 10 km × 10 km spatial resolution, based on empirical relationships between N_2O emission and total TN and SOC (*57*). They showed high background N_2O emissions in northeastern China and low background emissions in the North China Plain. It is noteworthy that their empirical relationships between N_2O emission and SOC (or TN) were the reverse of the pot experiment results of Huang et al. (*55*) and the statistical results of Liao (*54*). Gu et al. obtained empirical relationships between N_2O emission and TN (or SOC) from measurement of background emissions on 10 fields across China. The fields had not been fertilized for different numbers of years and had been cropped and managed differently (*58*). They used only TN (or SOC) to explain the observed variability in fluxes, and the effects of all other factors were ignored.

3.3. Estimation of N_2O Emissions from Croplands

Estimation of N_2O emission from croplands in China has been attempted frequently, using different methods and for different years. Three estimations have been made for the year 1995 and are therefore comparable. By regionalizing croplands in China and scaling-up representative field fluxes to a regional scale, Xing estimated N_2O emission from croplands in China in 1995 to be 398 Gg N (*59*). Using the DNDC (DeNitrification and DeComposition) model, Li et al. estimated N_2O emission from croplands in China to be 340 Gg N in 1995 (*60*). By following the 1996 IPCC Guidelines, but distinguishing emission factors between upland and rice paddy fields, Yan et al. estimated China's emission to be 476 Gg N in 1995 (*61*), i.e. higher than the other two estimates. In addition to the differences in estimation method, there are other two reasons that may explain this discrepancy. First, Yan et al. included emissions from permanent croplands and emissions in the fallow season, while these were not included by Xing (*59*). Second, there is a lack of statistics on the use of organic fertilizer, including animal manure and crop residues, and thus different expert judgments were used in these estimations.

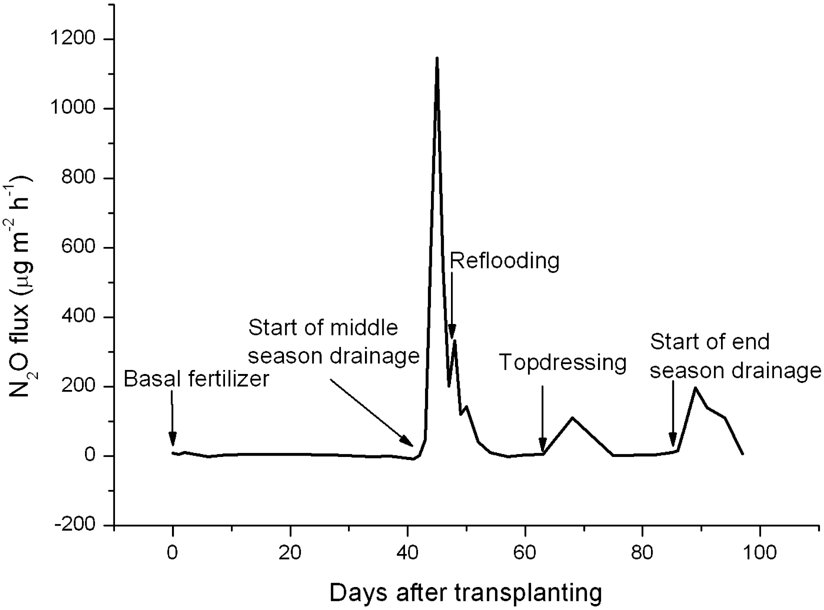


Figure 5. Typical seasonal pattern of N_2O emission from a rice paddy (modified from Yan et al. (49))

Recently, Zhang et al. compiled a dataset of fertilizer-induced N_2O emission factors in China (*62*). They calculated an average emission factor of 0.41% for rice from 195 emission factors, and an average emission factor of 1.05% for upland crops from 261 emission factors. Using these emission factors, and the 2006 IPCC Guidelines (*39*), they estimated a total N_2O emission of 288.4 Gg N for the year 2007. Given that background emission was not included in the IPCC 2006 Guidelines, this estimation is close to those of Xing (*59*) and Li et al. (*60*).

There are still large uncertainties in the fertilizer-induced emission factors in China. Many of the observations have not been carried out on a yearly basis. Another uncertainty in estimations often arises from the lack of reliable activity data, especially the use of organic fertilizers.

4. Organic C Storage in Cropland Soils and Changes

Soil is an important C pool, which plays a significant role not only in the budget of atmospheric CO_2, but also soil quality, particularly related to soil productivity. Due to the limitation of data availability, SOC storage in China was estimated mostly using the data from the Second National Soil Survey, conducted during the late 1970s to the early 1980s. Due to differences in land area, number of soil profiles, soil bulk density, and methods used for scaling from soil profiles up to the national scale, estimated SOC storage in the upper 100 cm of soils of China ranged from 50 (*63*) to 185 Pg C (*64*). Nevertheless, most estimates fell within a much narrower range: 69.1 (*65*) to 101.8 Pg C (*66*). Excluding the extreme low and high estimates, the average storage is 85.76 ± 10.49 Pg C with an SOC density of 9.55 ± 1.17 kg C m^{-2} for the average land area of 8.9821 × 10^6 km^2 in China. Using the CEVSA model, Li et al. estimated SOC storage in the upper 100 cm of Chinese soils to be 82.65 Pg C (*67*), which is very close to the average estimate obtained using soil survey data. Post et al. estimated that the average of SOC density in global soils was 10.8 kg m^{-2} and the total storage was 1395 Pg C (*68*), which fell in the lower range of estimated global SOC storage (*69*). The IPCC estimated the global average density to be 13.3 kg m^{-2} (*70*). Thus the SOC density of Chinese soils was lower than the average global SOC density. Yang et al. attributed the low SOC density in China to the large proportion of soils located in arid and semi-arid regions, the low percentage of forest coverage, intensive cultivation, and low return of crop residues into soils (*65*). In this section, we focus on the SOC storage and changes in croplands of China.

4.1. Organic C Storage in Cropland Soils

SOC storage in croplands in China has been intensively estimated by modeling or scaling up from soil profiles. Based on the dataset obtained from the Second National Soil Survey, Xie et al. estimated that the SOC storage in cropland soil was 12.98 Pg C, of which 2.91 Pg C was in paddy soils of 29.87 Mha, and 10.07 Pg C was in the upland soil of 125.89 Mha, including orchard plantations. The SOC storage in the plough layer was 0.82 Pg C in paddy soil with an average layer depth of 15.2 cm, and 3.07 Pg C in upland soil with an average layer depth of 19.4 cm (*71*). Applying the DNDC model, Tang et al. estimated that the SOC storage in cropland soil (0–30 cm) of 96.8 Mha was 3.97 Pg C in 1998, with SOC density of 4.1 kg C m^{-2} (*72*). They revised the area of cropland to 118 Mha and obtained a new estimate of the SOC storage of range 4.7–5.2 with an average of 4.95 Pg C in 2003. The SOC density was 3.9–4.4 kg C m^{-2} (*73*).

Due to large uncertainties in the area of croplands, variations in depth of plough layers, large spatial variations in SOC content, and different cropping systems and management, there are still very large uncertainties in the estimated SOC storage in croplands in China. Uncertainties also arise from the spatial resolution for estimating SOC storage. Zhang et al. compared the SOC storage in a red soil region of China estimated by unclassified grid-based mode, soil-type-based mode, land-use-pattern-based mode, and land-use-pattern–soil-type-based mode and found different uncertainties in the estimated SOC storage (*74*). They suggested that land-use patterns associated with soil-type modes was the best way to estimate SOC storage at a county level.

Despite uncertainties, some conceptions of SOC storage or density in cropland soils have been developed. Generally speaking, cultivation of natural soils leads to SOC loss, thus the SOC density of cropland soils is, on average, lower than those in forest and grassland soils (*71*). Taking the SOC density in natural soils as the original value before the reclamation, conversion of natural soils into cropland soils had led to 1.65 Pg C loss in the eastern China (*75*). At the national scale, the SOC lost by land-use change was estimated to be 2.48 Pg SOC in the last 300 years (*76*). In China, cultivation started thousands of years ago and almost all arable lands have been cultivated. Northeast China is one of the last reclaimed regions where large-scale reclamation started in the 1950s. Thus, the dynamics of SOC content after cultivation were mostly investigated in this region. The results showed that for the phaeozem enriched with organic matter, on average, it took 40 years of cultivation for SOC content to decrease to half of the original value (*77*). Nevertheless, cultivation of natural lands does not mean that SOC content decreases definitely. For natural soils with very low SOC content, the SOC content increases after conversion into cropland soils under reasonable management. For instance, the SOC content increased significantly after conversion of soils of marginal land into paddy fields in the subtropical region of China, particularly in the first 30 years (*67*). Therefore, the variations of SOC content in croplands are narrower than those in the natural lands (Table 1).

The SOC density of cropland soils varies with cropping systems. In the same region, the density was generally higher in paddy soils than in upland soils (*75*). The national average for the density in the plough layer of paddy soil (average depth 15.2 cm) was 2.76 kg C m^{-2}, higher than the 2.44 kg C m^{-2} for the plough layer of upland soil (average depth 19.4 cm; (*71*)). It is frequently found that SOC content increases in paddy soils even if aboveground biomass is removed (*79*). For flooding, there are banks surrounding a rice field, thus mitigating soil erosion and favoring the accumulation of organic C. Decomposition rate of organic materials is generally lower under the anaerobic conditions of flooded rice fields than under the aerobic conditions of uplands (*80*). The decomposition rate of SOC was found to be three times higher in aerobic compared to anaerobic conditions (*81*). However, opposite results have also been reported (*82*). The contradictory results are related, at least partially, to the duration of experiments – usually in short-term experiments the decomposition rate of SOC is faster in anaerobic than in aerobic conditions (*83*). The slower decomposition of SOC may be attributed to phenol enrichment under anaerobic conditions (*84*). The biomass produced and input *in situ* into soil (e.g. roots, root exudates and growth of algae) would also differ between rice fields and uplands, and this needs further quantification.

There is also a spatial variation of SOC density in croplands in China. On average, the lowest SOC content is found in north China, followed by northwest China, with the highest SOC content in Southwest China (Table 1). Semiarid and arid climates and severe soil erosion are the main causes of low SOC content in North and Northwest China. The highest SOC content in cropland soils in Southwest China is consistent with the highest SOC content in the non-cropland soils in the region; this agreement suggests that the highest SOC content in cropland soils was a residual effect of the original soils.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table 1. Topsoil SOC content of croplands and non-croplands and coefficients of variation (CV) in each region of China. Data source (*78*).

Region	*Non-croplands*			*Croplands*		
	No. of profiles	*SOC ($g\ kg^{-1}$)*	*CV (%)*	*No. of profiles*	*SOC ($g\ kg^{-1}$)*	*CV (%)*
East	137	22.5	82	324	13.6	52
Northeast	189	31.64	139	175	13.3	63
North	133	18.39	103	269	8	69
Mid-south	142	21.3	87	229	14.8	40
Northwest	194	21.65	142	248	10.19	77
Southwest	163	41.89	111	270	18.06	61

4.2. Changes in Organic C Storage in Cropland Soils

Because the Second National Soil Survey provided a unique dataset for estimating SOC density and storage at the national scale, research on changes in SOC storage in China usually took the SOC content or density or storage in the period of the survey during the late 1970s to the early 1980s as baselines. Long-term experiments were set up across the country in the 1980s to monitor changes in soil fertility due to the replacement of organic manure by chemical fertilizers. These long-term experiments and their SOC content data enabled the investigation at the national scale on change in SOC content in cropland soils. During the ‘Cultural Revolution’, food shortages and poverty caused farmers to harvest as much as possible and put less inputs into their land. These practices depleted the SOC, and so SOC content or density in croplands was believed to be low during the period of the Second National Soil Survey. Using the datasets of the First National Soil Survey, which was carried out in the early 1960s, and the Second National Soil Survey, Wang et al. estimated that the SOC in the upper 100 cm decreased by about 1 Pg in the period between the surveys (*85*).

Most long-term experiments set up in the 1980s and 1990s demonstrated that SOC content increased under the management prevailing at the time. A typical long-term experiment was set up in the Huang-Huai-Hai Plain of China in 1990 with seven treatments, i.e. neither chemical fertilizers nor organic manure application (CK); N, P and K were applied (NPK); N and P were applied without K (NP); N and K were applied without P (NK); P and K were applied without N (PK); organic compost was applied without inorganic fertilizers (ON); and half N supplied from inorganic fertilizer and the other half from compost (1/2ON). The cropping systems were typical of north China, i.e. summer maize and winter wheat, two crops per year. Aboveground biomass was removed from all treatments when harvesting. When the experiment started in 1989, the SOC content was only 4.48 ± 0.08 g C kg^{-1}. In 2003, SOC decreased only in the CK and NK treatments, in which P deficiency had inhibited crop growth, but increased by 4.5% in PK, 19% in NP, 27% in NPK, 58% in 1/2ON, and was almost doubled in ON (94%). The SOC content was significantly correlated with the organic C input from compost and roots calculated by the root/grain ratio (*86*). An increasing trend was also observed in paddy soils cropped with either single or double rice. A long-term experiment set up in 1980 in the Taihu Lake region, where the prevailing cropping system is summer rice and winter wheat, showed that the SOC content increased in all treatments including the control, in which no fertilizers were applied. SOC content was generally higher in the treatments using chemical fertilizers plus manure or rice straw compared to those using chemical fertilizers alone. A new equilibrium of SOC content was reached in treatments with manure amendments within about 10 years; however, in treatments without manure amendment equilibrium had not been reached within 25 years (*87*). Due to the compacted plough pan layer, increases in SOC content in paddy soils usually takes place in the plough layer alone (*88*).

Decreases in SOC contents were also observed in long-term experiments, particularly in treatments of unbalanced fertilization and in soils with high original SOC content (*89*, *90*)). Wang et al. collected topsoil SOC data of measurements over 1977 and 2006 from long-term Chinese agro-ecosystem experiments presented in 76 reports (*89*). The data set comprised 481 observations of SOC under different fertilization schemes at 70 experimental sites and covered 16 dominant soil types across 23 provinces of mainland China. They found an overall temporal increase in topsoil SOC content. The relative annual change in SOC content ranged from –0.14 to 0.60 with an average of 0.13 g kg^{-1} y^{-1} for upland soils, and from –0.12 to 0.70 with an average of 0.19 g kg^{-1} y^{-1} for rice paddies. The annual change in SOC content was affected by fertilization regimes: higher under organic fertilization and combined organic/inorganic fertilizations than chemical fertilizations; and higher under balanced chemical fertilizations with compound N, P and K fertilizers than unbalanced fertilizations such as N only, N plus P, and N plus K.

A meta-analysis of data on SOC changes reported in the literature demonstrated that generally during 1980–2000, SOC content increased in about 53–59%, remained essentially unchanged in 4–6%, and decreased in 30–31% of the total area of croplands in China (*91*). The change in SOC varied with spatial regions and soil types. For regions, SOC content increased in East and North China, but decreased in Northeast China; for soil types, SOC content increased in paddy soils and fluvo-aquic soils, but decreased in phaeozem.

An increase in SOC storage in cropland soils in China was estimated by analyzing the data on SOC content from regional soil surveys, inventories and long-term experiments across the country. Huang and Sun demonstrated a general trend of increasing topsoil SOC (300–400 Tg C) estimated roughly for all of China's croplands during 1980–2000, using observation data from publications (*91*). Xie et al estimated a topsoil SOC stock increase of 23 Tg C y^{-1} in China's croplands during the last two decades, using data from a small number of observations collected from 84 papers available in Chinese journals (*71*). Yu et al. used an artificial neural network model to link SOC change to six parameters, i.e. latitude, longitude, elevation, soil and land use type, original SOC in early 1980s and estimated an increase of 260 Tg C in the period 1980–2000 in the top 20 cm (*92*). Using the DNDC model, and climate and agricultural conditions for 1990, Li et al. estimated that China's croplands lost 95 Tg C, or 1.6% of their SOC (to a depth of 30 cm) per year (*93*). By using the same model, Tang et al. claimed that high rates of SOC losses occurred in the croplands with the most common cropping patterns in China (*73*).

Yan and Cai developed a scheme to compare the changes in SOC content in croplands of China by direct measurements at two time points (*94*). Statistical analysis of the SOC data from the Second National Soil Survey indicated that, with SOC content data of 1250 soil profiles, it would be possible to detect an overall SOC change of 5% in Chinese croplands with 95% confidence. Then Yan et al. collected 1394 cropland soil profiles over all the country in 2007–2008 and directly compared the SOC contents of these soil profiles with those from the Second National Soil Survey: the average SOC content in the 0–20-cm soil layer increased from 11.95 in 1979–1982 to 12.67 g kg^{-1} in 2007–2008, averaging 0.22% y^{-1} (*95*). The largest increase of SOC occurred in Calcaric Fluvisols and Fluvisols, both mainly distributed in the Yellow River reaches and with low original SOC contents; and in Anthrosols which dominate the paddy soils. SOC loss also occurred in northeast China.

4.3. Factors Driving Changes in Organic C Storage

Low SOC content in the early 1980s created potential for increasing SOC content in cropland soils in China with increased organic C input. It is well known that the rate of increase of SOC content slows generally with SOC accumulation in soils because of a corresponding increased decomposition rate (*86*). The change in SOC was closely correlated with the initial SOC content (*92*, *95*). Li and Wu investigated the changes of SOC in paddy soils in subtropical China from the 1980s and found a negative relationship between the change in SOC content and the initial SOC content. If the initial SOC content was > 19.0 g C kg^{-1}, the content was more likely to decrease; while it was more likely to increase if the initial content was < 19.0 g C kg^{-1} (*96*).

Organic C input into croplands increased, compared to before the 1980s. SOC change is the net balance of organic C decomposition and new organic C input. The increase in organic C input was mainly from two sources: increased crop yields and increased residues retained in fields. Mainly due to the increased use of chemical fertilizers and achievements in plant breeding, the national average yields of rice, maize and wheat increased by 53, 76 and 153%, respectively, during 1980–2007 (*1*). C input through roots, root exudates, stubble, and crop residue would likely have greatly increased, although probably not proportionately to crop yield since the harvest index (proportion of yield to total plant aboveground biomass) has also increased. Traditionally, crop straws were fully used by farmers, e.g. as fuel for cooking, bedding materials and feed for livestock. The ash of burned crop residues and animal wastes were returned to croplands as fertilizers. At that time, crop residues had high value to farmers and rarely remained in fields after harvesting. With improved economic situations, wide use of commercial energy in the countryside and the development of commercial animal feeds, the traditional use of crop residues has decreased dramatically and the surplus is increasing. Thus, field burning of crop residues occurs frequently; however, incorporation of crop residues into soils is also increasing. A survey conducted in 15 provinces showed that 25.5% of crop straw produced was incorporated into soils in 1999 and the fraction increased to 37.3% in 2000 (*97*).

Conservation tillage is expanding, particularly in North China. At a regional scale, zero tillage was practiced on 4.12 Mha of croplands, concentrated mostly in regions such as Heilongjiang, Hebei, Henan, Jiangsu and Anhui Provinces, and was estimated to sequester 0.8 Tg C y^{-1} (*98*).

Estimations showed that SOC was lost as a whole in the cropland soils in northeast China without exception (*92*, *93*, *95*). Firstly, Northeast China has a relatively short cultivation history and the original soils such as phaeozem contain high SOC contents. The SOC contents of these newly reclaimed soils have not yet reached a new, lower equilibrium. Secondly, newer organic C inputs from crop growth in this region is less than the national average, reflected in the net primary production estimates from crop production (*99*). The low net primary production can be partially attributed to the low crop index of 0.89 in this region, compared with the national average of 1.21 (*95*). Thirdly, cultivation promotes soil erosion. The phaeozem region of northeast China has become the most vulnerable region for potential erosion in China and in some parts the parent loess material is exposed (*100*). SOC content decreases with erosion of topsoils, which have high SOC contents.

5. Mitigation Options and Potential

With the accumulation of field measurements across the country and improved knowledge, many factors affecting CH_4 and N_2O emissions from croplands and C sequestration into cropland soils have been identified. Based on these achievements, it is thought that greenhouse gas emissions from croplands in China can be significantly mitigated through appropriate management (*36*, *98*, *101*). However, the following should be taken as principles for applying options in mitigating CH_4 and N_2O emissions from and sequestering C into cropland soils. First, any options should not endanger food security and farmers' benefits. Second, the interactions of options and the trade-off relationships of CH_4, N_2O emissions and soil C sequestration should be taken into account.

5.1. Mitigation Options for CH_4 Emission from Rice Paddies

CH_4 is the terminal product of soil reduction in the succession of oxidation–reduction. In principle, any factors or practices able to retard soil reduction or reduce organic substrates will mitigate CH_4 emissions from rice fields. Among all factors, water regimes and organic substrates and their combination are crucial for controlling CH_4 emissions from rice fields.

Water regimes are important not only during the rice growing period, but also in the off-rice season, in determining CH_4 emissions from rice fields. Flooding, or at least water-saturation of soil, is a prerequisite but not sufficient condition for CH_4 production, since CH_4 is a terminal product of soil reduction. Only when active oxidants such as oxygen, NO_3^-, Mn^{4+}, Fe^{3+} and SO_4^{2-} are consumed and anaerobic conditions have developed in soil (at least at microsites) is detectable amounts of CH_4 produced, given available organic substrates. The history of soil moisture before flooding for growing rice determines the duration of the development of anaerobic conditions after flooding (*102*), thus affecting CH_4 emissions from rice fields during the rice growing period. Since year-round flooding is the extreme water regime most favorable for CH_4 production, the largest CH_4 emissions were observed in rice fields in China that experienced these conditions (*29*). CH_4 emission also occurs if a rice field is flooded in the off-rice season (*29*). Therefore, draining rice fields sufficiently in the off-rice season will mitigate CH_4 emission in the off-rice season and also significantly during the rice growing period. Shiratori et al. (*103*)found that subsurface drainage of water-logged rice fields in Japan in the off-rice season mitigated CH_4 emissions significantly during the rice growing period. They established a linear relationship between soil moisture before flooding for rice transplanting and CH_4 emissions in the following rice-growing period. For various reasons, such as poor drainage in topographic depressions, lack of well-developed irrigation systems to ensure flooding of the rice field for rice transplanting, and poor management in the off-rice season, there is about 2.7–4.0 Mha of rice fields flooded year-round in China, and this is estimated to contribute CH_4 emission of 2.44 Tg y^{-1} (*104*). If flooding of some rice fields in the off-rice season is only due to poor management then lowering CH_4 emissions is relatively easy. For year-round flooded rice fields due to poor drainage and irrigation conditions, mainly distributed in hilly and mountainous areas in South and Southwest China, local farmers have developed a ridged cultivation system, in which ridges are built and maintained before rice transplanting every year. Rice is planted in both sides of the ridges, flooded water is kept in ditches, and the water level is raised to the top of ridges during the rice growing period and lowered to a certain level in the off-rice season. This practice raises soil redox-potential in the ridges and reduces CH_4 emissions by about 33% (*19*). Xu and Hosen demonstrated that keeping the soil water content in the range of 38–59% water holding capacity in the fallow season is important to lower CH_4 emissions (*105*).

It has been well documented that drainage in mid-season during the rice growing period mitigates CH_4 emission. As mentioned previously, Yan et al. found that, on average, CH_4 emission from rice fields with mid-season drainage was 53% that from continuously flooded fields. The effectiveness of mid-season drainage depends on the number of drainage events, and the timing and duration of each drainage event (*13*). Mid-season drainage has been widely practiced in China for > 30 years. The original objective of mid-season drainage was to control the number of rice tillers and promote root growth, and thus increase rice yield, rather than to mitigate CH_4 emission. The potential of this practice to mitigate CH_4 emissions from rice fields in China is expected to be limited since only for a small area of rice fields is mid-season drainage not currently practiced. Furthermore, a great attention is needed on the trade-off relationship between CH_4 and N_2O emissions from rice fields. Very large N_2O emissions were observed from rice fields with soil moisture close to water-saturation (*47*, *50*), although this water regime significantly inhibited CH_4 emissions (*50*).

Increases in supplies of organic substrate under flooded conditions stimulates CH_4 emission. Therefore, amendments of organic manure, and incorporation of crop straw and green manure usually increase CH_4 emissions from rice fields. However, these practices may be essential for maintaining soil fertility. It has been demonstrated that at the same amount of organic C input, the CH_4 emissions induced by compost and biogas residues were less than that by crop straw (*106*). Incorporation of crop straw in the off-rice season when fields are drained stimulates CH_4 emissions less than incorporation just before rice transplanting (*106*, *107*). CH_4 emissions induced by straw incorporation varies also with the patterns of straw incorporation (*108*). So, selecting an appropriate incorporation pattern should reduce the stimulation of CH_4 emissions. In the case of straw incorporation just before transplanting, practicing mid-season drainage earlier than usual can also reduce the stimulation of CH_4 emission (*37*).

CH_4 emissions from paddy fields are affected by planting density. Higher rice planting density leads to higher CH_4 emission fluxes because a high-density crop has more stems, leaves and roots, which speed up transmission and emission of CH_4. To ensure good crop yield, the rice planting density can be adjusted only within a very limited range, and hence there is limited potential of reducing planting density to reduce CH_4 emissions. The effect of rice variety on paddy CH_4 emissions varies. Ding et al. found that CH_4 emission was positively related to rice plant height, and the emission from paddy fields grown with tall-stalk rice (120-cm plant height) was 2.9 times that from fields sown with dwarf rice (90-cm height) (*109*). However, crop yield is the current priority for selection of rice varieties.

Application of electron acceptors such as NO_3^-- and SO_4^+-containing fertilizers, and Fe and Mn oxides mitigates CH_4 emissions from rice fields (*23*, *106*, *110*); however, they are less feasible. Chemicals that inhibit the activities of methanogenic bacteria depress CH_4 emissions during the rice growing period. Commonly used nitrification inhibitors can mitigate CH_4 emissions from rice fields (*112*). It has also been reported that CH_4 emissions from rice–duck systems are less than from pure rice fields in south China (*113*).

5.2. Mitigation Options for N_2O Emission from Croplands

China currently consumes about one third of global N-fertilizers and consumption is predicted to increase. Fundamentally, mitigation of N_2O emissions from croplands relies on enhancing N-use efficiency, thus reducing N-fertilizer application rate under the premise of getting high crop yields. It was estimated that if N-use efficiency could be enhanced from 31 ± 11% for rice, 33 ± 13% for wheat, and 31 ± 11% for maize cultivation in the late 1990s to 50% for these crops, 6.6 Tg of synthetic N could be cut per year, and direct N_2O emission from croplands together with CO_2 emission from the industrial production and transport of synthetic N could be reduced by 39%, equivalent to 60 Tg CO_2 y^{-1} (*101*). The obstacles to enhancing N-use efficiency are awareness, economics, labor costs and technology, rather than knowledge. For example, it is well documented that deep application of N-fertilizer enhances N-use efficiency; however, the deep application of topdressing N-fertilizer is still very technologically difficult.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Similar to CH_4 emission, water regime is also a crucial factor for N_2O emission from cropland. In contrast with CH_4 emission, which is favored by continuous flooding or water-saturation, N_2O emission is favored by alternately wet and dry conditions (*114*, *115*). With stable soil moisture, nitrification of NH_4^+ as fertilizers applied to upland soils is usually completed in 1–2 weeks. Wetting soil stimulates denitrification of NO_3^-, the product of nitrification. Precipitation is the main cause of soil moisture change, hence a significant correlation was established between precipitation and N_2O emission from croplands across China (*116*). For rice fields, N_2O emission factor is raised by the number of mid-season drainage events (*117*), although this practice mitigates CH_4 emission (*61*). Avoiding unnecessary irrigation of uplands and unnecessary drainage of rice fields is as important as avoiding excessive application of N-fertilizers in mitigation of N_2O emissions from croplands.

Associated applications of urease inhibitor or nitrification inhibitor with urea and NH_4^+-containing fertilizers inhibits N transformation, thus mitigating N_2O emission. A meta-analysis showed that compared with conventional fertilizers, the fertilizers containing nitrification inhibitor reduced N_2O emissions by 38%; however, fertilizers containing urease inhibitors did not significantly reduce N_2O emission (*118*). For rice production, application of these inhibitors with topdressing at tillering stage producing the best mitigation effects (*112*).

Replacing conventional N-fertilizers, such as urea and NH_4^+-bicarbonate with slow-release or controlled-release N-fertilizers has been suggested for mitigating N_2O emissions from croplands (*119*). Polymer-coated fertilizers significantly reduced N_2O emissions by 35% (*118*).

5.3. Options for Soil C Sequestrations

As discussed in section 4, SOC storage in Chinese croplands has most likely increased in the last three decades. A new equilibrium content of SOC will be reached within a certain period of introducing a new practice. Wang et al. summarized the long-term experiments conducted across the country and concluded that the effects of specific rational fertilizations on SOC increase persisted for 15 years in uplands and 20 years in rice paddies (*89*). From a long-term experiment conducted in Yangtze Delta Plain of China, Rui et al. concluded that crop residue additions and animal manure applications enhanced SOC only over periods of about 20 and 40 years (*120*). So, the question is – is there potential in cropland soils for further C sequestration in China after continuous increases over 30 years?

SOC content is expected to increase by either increased organic C input or decreased SOC loss or both. To increase crop yields through proper management and breeding is one measure to increase organic input into soil, because root exudates and crop residues return increase proportionally to growth. However, if high yield was achieved by increases in chemical fertilizers, as estimated by Lu et al. (*98*), the contribution of soil C sequestration to mitigation of climate change would be a trade-off at least partially by CO_2 emission from fertilizer production and transportation and N_2O emission increase due to chemical fertilizer (*121*). Practices of straw incorporation are a priority option for increasing SOC density in croplands in China. Although field burning of crop straws is officially banned, it still occurs widely. Yan et al. estimated that 19% of the total crop residue is burned in the field (*122*). If the burned crop straws could be incorporated into soils, there is significant potential for increasing SOC density of croplands. However, direct incorporation of crop straw into rice fields, particularly before rice transplanting, may stimulate CH_4 emissions and exceed straw-induced C sequestration in terms of global warming potential. Using the IPCC Guidelines, Lu et al. estimated that while the incorporation of half of rice straw into rice paddies in China would sequester 10.48 Tg y^{-1} of C in paddy soils (38.1 Tg CO_2-equivalents y^{-1}), the CH_4 emission from the rice paddies would increase by 3.32 Tg CH_4 y^{-1} (82.95 Tg CO_2-equivalents y^{-1}), which was 2.16 times of the mitigation from C sequestration in rice paddies (*123*). Incorporation of crop straw in the off-rice season in the cropping system of rice and upland winter crop could reduce straw-induced CH_4 emission. However, a long-term experiment conducted in the cropping system of rice and winter wheat showed that incorporation of crop straw during the winter wheat-growing period reduced wheat yields (*87*). Therefore, straw incorporation should not be encouraged in rice-based agroecosystems.

Many reports have shown that conservation tillage, including zero and minimum tillage, is an effective option for enhancing SOC content in croplands in arid and semi-arid regions of China. Conservation tillage associated with straw cover is more effective in sequestering C into soil (*124–126*). Soil in arid and semi-arid regions of China is suffering from wind erosion. Conservation tillage associated with straw-cover reduces this wind erosion effectively, thus stabilizing surface soil and increasing SOC content in the topsoil. However, the feasibility and effectiveness of conservation tillage in sequestering organic C in humid subtropical China needs further research.

Currently, options for sequestering soil C and managing organic wastes through producing biochar and then applying this to soil are being intensively investigated in China. Yet, it is too early to review the feasibility and effectiveness of these measures on mitigating climate change, soil fertility and sustainability.

References

1. FAOSTAT, (Statistical Database of the Food and Agricultural Organization of the United Nations). Available online at http://faostat.fao.org/site/405/default.aspx. 2010.
2. IRRI, I. R. R. I., http://beta.irri.org/solutions/index.php?option=com_content&task=view&id=250. 2011.
3. Yan, H. M.; Y., L. J.; Cao, M. K. *Acta Geogr. Sin.* **2005**, *60*, 559−566. (In Chinese).
4. Winchester, J. W.; Fan, S. M.; Li, S. M. *Water Air Soil Pollut.* **1988**, *37* (1), 149–155.
5. Khalil, M. A. K.; Rasmussen, R. A.; Wang, M. X.; Ren, L. X. *Environ. Sci. Technol.* **1991**, *25* (5), 979–981.

6. Wang, S. B.; Song, W. Z.; Su, W. H.; Zeng, J. H.; Zhang, Y. M.; Wang, Z. P. *Agro-environ. Prot.* **1994**, *13* (5), 210−212. (In Chinese with English abstract).
7. Yan, X. Y.; Yagi, K.; Akiyama, H.; Akimoto, H. *Global Change Biol.* **2005**, *11* (7), 1131–1141.
8. Tao, Z.; Du, D. D.; Zhou, Y.; Mai, G. X.; Liu, X. W. *Rural Eco-Environ.* **1994**, *10* (3), 1−5. (In Chinese with English abstract).
9. Wang, M. X.; Shangguan, X. J.; Shen, R. X.; Wang, Y. S.; Wassmann, R.; Renenberg, H.; Seiler, W.; Xie, X. L.; Wang, W. D. *China Agric. Meteorol.* **1995**, *16* (2), 1−5. (In Chinese with English abstract).
10. Zou, J. W.; Huang, Y.; Zong, L. G.; Wang, Y. S.; Sass, R. L. *Chin. J. Environ. Sci.* **2003**, *24* (4), 7−12. (In Chinese with English abstract).
11. Qin, X. B.; Li, Y. E.; Liu, K. Y.; Wan, Y. F. *Trans. CSAE* **2006**, *22* (7), 143−148. (In Chinese with English abstract).
12. Ma, J.; Li, X. L.; Xu, H.; Han, Y.; Cai, Z. C.; Yagi, K. *Aust. J. Soil Res.* **2007**, *45* (5), 359–367.
13. Yan, X. Y.; Cai, Z. C.; Ohara, T.; Akimoto, H. *J. Geophys. Res. Atmos.* **2003**, *108* (D16).
14. Xiao, X. P.; Wu, F. L.; Huang, F. Q.; Li, Y.; Sun, G. F.; Hu, Q.; He, Y. Y.; Chen, F.; Yang, G. L. *Res. Agric. Modern.* **2007**, *28* (5), 629-632. (In Chinese with English abstract).
15. Ma, J.; Xu, H.; Yagi, K.; Cai, Z. C. *Plant Soil* **2008**, *313* (1-2), 167–174.
16. Xu, H.; Cai, Z. C.; Li, X. P. *Acta Pedolog. Sin.* **2000**, *37* (1), 69−76. (In Chinese with English abstract).
17. Jia, Z. J.; Cai, Z. C.; Xu, H.; Li, X. P. *Plant Soil* **2001**, *230* (2), 211–221.
18. Li, X. L.; Xu, H.; Cao, J. L.; Cai, Z. C.; Yagi, K. *Soils* **2007**, *39* (2), 238−242. (In Chinese with English abstract).
19. Cai, Z. C.; Tsuruta, H.; Gao, M.; Xu, H.; Wei, C. F. *Global Change Biol.* **2003**, *9* (1), 37–45.
20. Kang, G. D.; Cai, Z. C.; Feng, Z. H. *Nutri. Cycl. Agroecosys.* **2002**, *64* (1-2), 95–100.
21. Cai, Z. C.; Xu, H.; Lu, W. S.; Liao, Z. W.; Zhang, J. G.; Wei, C. F.; Xie, D. T. *Chin. J. Appl. Ecol.* **1998**, *9* (2), 171−175. (In Chinese with English abstract).
22. Chen, G. X.; Huang, G. H.; Huang, B.; Wu, J.; Yu, K. W.; Xu, H.; Xue, X. H.; Wang, Z. P. *Chin. J. Appl. Ecol.* **1995**, *6* (4), 378−382. (In Chinese with English abstract).
23. Cai, Z. C.; Xing, G. X.; Yan, X. Y.; Xu, H.; Tsuruta, H.; Yagi, K.; Minami, K. *Plant Soil* **1997**, *196* (1), 7–14.
24. Zou, J. W.; Huang, Y.; Jiang, J. Y.; Zheng, X. H.; Sass, R. L. *Global Biogeochem. Cycl.* **2005**, *19* (2).
25. Lin, K. F.; Xiang, Y. L.; Jiang, D. B.; Hu, Q. L.; Li, Z. H.; Du, D. D.; Tao, Z. *Agro-environ. Prot.* **2000**, *19* (5), 267−270. (In Chinese with English abstract).
26. Xu, H.; Cai, Z. C. *Rural Eco-Environ.* **1999**, *15* (1), 10−13. (In Chinese with English abstract).

27. Ma, J.; Xu, H.; Han, Y.; Cai, Z. C.; Yagi, K. *Soils* **2007**, *39* (6), 859−862. (In Chinese with English abstract).
28. Shuangguan, X. J.; Wang, M. X.; Shen, R. X. *Adv. Earth Sci.* **1993**, *8* (5), 13−21. (In Chinese with English abstract).
29. Cai, Z. C.; Tsuruta, H.; Minami, K. *J. Geophys. Res., [Atmos.]* **2000**, *105* (D13), 17231–17242.
30. Wassmann, R.; Schütz, H.; Papen, H.; Rennenberg, H.; Seiler, W.; Aiguo, D.; Renxing, S.; Xingjian, S.; Mingxing, W. *Biogeochemistry* **1993**, *20* (2), 83–101.
31. Yao, H.; Zhuang, Y. B.; Chen, Z. L. *Global Biogeochem. Cycl.* **1996**, *10* (4), 641–649.
32. Cai, Z. C. *Nutri. Cycl. Agroecosys.* **1997**, *49* (1-3), 171–179.
33. Cao, M.; Dent, J. B.; Heal, O. W. *Agri. Ecosys. Environ.* **1995**, *55* (2), 129–137.
34. Huang, Y.; Sass, R. L.; Fisher, F. M. *Global Change Biol.* **1998**, *4* (8), 809–821.
35. Matthews, R. B.; Wassmann, R.; Knox, J. W.; Buendia, L. V. *Nutri. Cycl. Agroecosys.* **2000**, *58* (1), 201–217.
36. Yan, X. Y.; Akiyamasmith, H.; Yagi, K.; Akimoto, H. *Global Biogeochem. Cycl.* **2009**, *23*.
37. Cai, Z. C.; Xu, H.; Ma, J. *Methane and Nitrous Oxide Emissions from Rice-Based Ecosystems*; Press of China Science and Technology University: Hefei, 2009.
38. Smith, C. J.; Brandon, M.; Patrick, J. W. H. Nitrous oxide emission following urea-N fertilization of wetland rice. *Soil Sci. Plant Nutr.* **1982**, *28*, 161–171.
39. IPCC, *2006 IPCC guidelines for national greenhouse gas inventories volume 4: Agriculture, forestry, and other land use.* OECD: Paris, 2007
40. Yu, K. W.; Chen, G. X.; Yang, S. H.; Wu, J.; Huang, B.; Huang, G. H.; Xu, H. *Chin. J. Appl. Ecol.* **1995**, *6* (4), 387−391. (In Chinese with English abstract).
41. Yang, L.; Cai, Z. *Soil Biol. Biochem.* **2005**, *37* (6), 1205–1209.
42. Xiang, H. Y.; Zhu, B.; Kuang, F. H.; Li, K.; Wang, Y. Y.; Zheng, X. H. *Acta Sci. Circumstant.* **2007**, *27* (3), 413− 420. (In Chinese with English abstract).
43. Ding, W. X.; Cai, Y.; Cai, Z. C.; Yagi, K.; Zheng, X. H. *Sci. Total Environ.* **2007**, *373* (2-3), 501–511.
44. Ruan, L. M.S. thesis, Hubei, China, 2007.
45. Liang, D. L.; Tong, Y. A.; Emteryd, O.; Ma, L. Y. *J. Northwest Sci-tech. Univ. Agric. For.* 2002, *30* (2), 73−77. (In Chinese).
46. Huang, S. H.; Jiang, W. W.; Lu, J.; Cao, J. M. *China Environ. Sci.* **2005**, *25* (5), 540−543. (In Chinese with English abstract).
47. Zheng, X.; Wang, M.; Wang, Y.; Shen, R.; Gou, J.; Li, J.; Jin, J.; Li, L. *Chemosphere: Global Change Sci.* **2000**, *2* (2), 207–224.
48. Lin, S.; Iqbal, J.; Hu, R.; Wu, J.; Zhao, J.; Ruan, L.; Malghani, S. *Atmos. Environ.* **2011**.
49. Yan, X.; Du, L.; Shi, S.; Xing, G. *Biol. Fertil. Soils* **2000**, *32* (1), 60–66.
50. Xu, Y. C.; Shen, Q. R.; Li, M. L.; Dittert, K.; Sattelmacher, B. *Biol. Fertil. Soils* **2004**, *39* (3), 215–217.

51. Zheng, X. H.; Wang, M. X.; Wang, Y. S.; Shen, R. X.; Shangguan, X. J.; Jin, J. S.; Li, L. T. *Sci. Atmospher. Sin.* **1997**, *21*, 231−237. (In Chinese with English abstract).
52. Xu, H.; Xing, G. X.; Cai, Z. C.; Tsuruta, H. *Agro-environ. Prot.* **2000**, *19* (1), 1−3. (In Chinese with English abstract).
53. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. *Global Biogeochem. Cycl.* **2002**, *16* (4).
54. Liao, Q. J. H. Ph. D. thesis, Institute of Soil Science, Chinese Academy of Sciences, Nanjing, 2010.
55. Huang, Y.; Jiao, Y.; Zong, L. G.; Wang, Y. S.; Sass, R. L. *Biol. Fertil. Soils* **2002**, *36* (6), 411–417.
56. Stevens, R. J.; Laughlin, R. J.; Malone, J. P. *Soil Biol. Biochem.* **1998**, *30* (8-9), 1119–1126.
57. Gu, J. X.; Zheng, X. H.; Zhang, W. *Plant Soil* **2009**, *320* (1-2), 307–320.
58. Gu, J.; Zheng, X.; Wang, Y.; Ding, W.; Zhu, B.; Chen, X.; Zhao, Z.; Shi, Y.; Zhu, J. *Plant Soil* **2007**, *295* (1), 53–65.
59. Xing, G. X. *Nutri. Cycl. Agroecosys.* **1998**, *52* (2-3), 249–254.
60. Li, C. S.; Zhuang, Y. H.; Cao, M. Q.; Crill, P.; Dai, Z. H.; Frolking, S.; Moore, B, I. I. I.; Salas, W.; Song, W. Z.; Wang, X. K. *Nutri. Cycl. Agroecosys.* **2001**, *60* (1-3), 159–175.
61. Yan, X. Y.; Akimoto, H.; Ohara, T. *Global Change Biol.* **2003**, *9* (7), 1080–1096.
62. Zhang, Q.; Ju, X. T.; Zhang, F. S., *Chin. J. Eco-Agric.* **2010**, *18* (1), 7-13. (In Chinese with English abstract).
63. Fang, J.; Liu, G.; Xu, S. Carbon reservoir of terrestrial ecosystem in China. *In Monitoring and Relevant Processes of Greenhouse Gas Concentration and Emission*; China Environmental Sciences Publishing House: Beijing, 1996; pp 109−128. (In Chinese).
64. Pan, G. X. *Sci. Technol. Bull.*. **1999**, *15*, 330−332. (In Chinese).
65. Yang, Y. H.; Mohammat, A.; Feng, J. M.; Zhou, R.; Fang, J. Y. *Biogeochemistry* **2007**, *84* (2), 131–141.
66. Wang, X. Q.; Zhou, C. H. *Geogr. Res.* **1999**, *18*, 349-356. (In Chinese).
67. Li, Z. P.; Zhang, T. L.; Chen, B. Y.; Yin, R. L.; Shi, Y. Q. *Acta Pedol. Sin.* **2003**, *40*, 344−352. (In Chinese with English abstract).
68. Post, W. M.; Emanuel, W. R.; Zinke, P. J.; Stangenberger, A. G. *Nature* **1982**, *298* (5870), 156–159.
69. Batjes, N. H. *Eur. J. Soil Sci.* **1996**, *47* (2), 151–163.
70. IPCC, *Climate Change 2001:The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA, 2001; p 881.
71. Xie, Z. B.; Zhu, J. G.; Liu, G.; Cadisch, G.; Hasegawa, T.; Chen, C. M.; Sun, H. F.; Tang, H. Y.; Zeng, Q. *Global Change Biol.* **2007**, *13* (9), 1989–2007.
72. Tang, H. J.; Qiu, J. J.; Van Ranst, E.; Li, C. S. *Geoderma* **2006**, *134* (1-2), 200–206.

73. Tang, H. J.; Qiu, J. J.; Wang, L. G.; Li, H.; Li, C. S.; van Ranst, E. *Sci. Agric. Sin.* **2010**, *9* (5), 704−712. (In Chinese with English abstract).
74. Zhang, Z. Q.; Yu, D. S.; Shi, X. Z.; Weindorf, D. C.; Wang, X. X.; Tan, M. Z. *Soil Tillage Res.* **2010**, *110* (1), 2–7.
75. Cai, Z. C. *Water Air Soil Poll.* **1996**, *91* (3-4), 383–393.
76. Ge, Q. S.; Dai, J. H.; He, F. N.; Pan, Y.; Wang, M. M. *Sci. China Ser. D* **2008**, *51* (6), 871−884. (In Chinese with English abstract).
77. Xing, G.; Yan, L.; Wang, J. H.; Guan, L. Z. *Chin. J. Soil Sci.* **2004**, *33*, 332−335. (In Chinese with English abstract).
78. Wu, L. Z. Ph.D. thesis, Nanjing, China, 2007.
79. Pampolino, M. F.; Laureles, E. V.; Gines, H. C.; Buresh, R. J. *Soil Sci. Soc. Am. J.* **2008**, *72* (3), 798–807.
80. Bird, J. A.; van Kessel, C.; Horwath, W. R. *Soil Sci. Soc. Am. J.* **2003**, *67* (3), 816–816.
81. DeBusk, W. F.; Reddy, K. R. *Soil Sci. Soc. Am. J.* **1998**, *62* (5), 1460–1468.
82. Takahashi, S.; Ueno, H.; Yamamuro, S. *Plant Soil* **2004**, *259* (1-2), 307–314.
83. Shibu, M. E.; Leffelaar, P. A.; Van Keulen, H.; Aggarwal, P. K. *Geoderma* **2006**, *137* (1-2), 1–18.
84. Olk, D. C.; Jimenez, R. R.; Moscoso, E.; Gapas, P. *Soil Sci. Soc. Am. J.* **2009**, *73* (3), 943–951.
85. Wang, S. Q.; Tian, H. Q.; Liu, J. Y.; Pan, S. F. *Tellus, Ser. B* **2003**, *55* (2), 416–427.
86. Cai, Z. C.; Qin, S. W. *Geoderma* **2006**, *136* (3-4), 708–715.
87. Shen, M. X.; Yang, L. Z.; Yao, Y. M.; Wu, D. D.; Wang, J. G.; Guo, R. L.; Yin, S. X. *Biol. Fertil. Soils* **2007**, *44* (1), 187–200.
88. Li, Z. P.; Liu, M.; Wu, X. C.; Han, F. X.; Zhang, T. L. *Soil Tillage Res.* **2010**, *106* (2), 268–274.
89. Wang, C. J.; Pan, G. X.; Tian, Y. G.; Li, L. Q.; Zhang, X. H.; Han, X. J. *Sci. China, Ser. C: Life Sci.* **2010**, *53* (7), 858–867.
90. Zhao, L. J.; Han, X. Z.; Wang, S. Y.; Liu, H. X.; Li, H. B.; Miao, S. J.; Wang, F. *Chin. J. Appl. Ecol.* **2006**, *17* (5), 817−821. (In Chinese with English abstract).
91. Huang, Y.; Sun, W. *Chin. Sci. Bull.* **2006**, *51*, 1785–1803.
92. Yu, Y. Y.; Guo, Z. T.; Wu, H. B.; Kahmann, J. A.; Oldfield, F., *Global Biogeochem. Cycl.* **2009**, *23*.
93. Li, C. S.; Zhuang, Y. H.; Frolking, S.; Galloway, J.; Harriss, R.; Moore, B.; Schimel, D.; Wang, X. K. *Ecol. Appl.* **2003**, *13* (2), 327–336.
94. Yan, X. Y.; Cai, Z. C. *Soil Sci. Plant Nutri.* **2008**, *54* (5), 819–825.
95. Yan, X.; Cai, Z.; Wang, S.; Smith, P. *Global Change Biol.* **2011**, doi: 10.1111/j.1365-2486.2010.02286.x.
96. Li, Z. P.; Wu, D. F. *Acta Pedolog. Sin.* **2006**, *43*, 46−52. (In Chinese with English abstract).
97. Han, L. J.; Yan, Q. J.; Liu, X. Y.; Hu, J. Y. *Trans. Chin. Soc. Agri. Eng.* **2002**, *18*, 87−91. (In Chinese with English abstract).
98. Lu, F.; Wang, X. K.; Han, B.; Ouyang, Z. Y.; Duan, X. N.; Zheng, H.; Miao, H. *Global Change Biol.* **2009**, *15* (2), 281–305.

99. Huang, Y.; Zhang, W.; Sun, W. J.; Zheng, X. H. *Ecol. Appl.* **2007**, *17* (3), 692–701.
100. Fan, H. M.; Cai, Q. G.; Wang, H. S. *J. Soil Water Conserv.* **2004**, *18* (2), 66–70.
101. Huang, Y.; Tang, Y. H. *Global Change Biol.* **2010**, *16* (11), 2958–2970.
102. Xu, H.; Cai, Z. C.; Tsuruta, H. *Soil Sci. Soc. Am. J.* **2003**, *67* (4), 1147–1157.
103. Shiratori, Y.; Watanabe, H.; Furukawa, Y.; Tsuruta, H.; Inubushi, K. *Soil Sci. Plant Nutri.* **2007**, *53* (4), 387–400.
104. Cai, Z. C.; Kang, G. D.; Tsuruta, H.; Mosier, A. *Pedosphere* **2005**, *15* (1), 66–71.
105. Xu, H.; Hosen, Y. *Plant Soil* **2010**, *335* (1-2), 373–383.
106. Wassmann, R.; Lantin, R. S.; Neue, H. U.; Buendia, L. V.; Corton, T. M.; Lu, Y. *Nutri. Cycl. Agroecosys.* **2000**, *58* (1), 23–36.
107. Cai, Z.; Xu, H., Options for mitigating CH4 emissions from rice fields in China. In *Hayashi (ed) Material Circulation through Agro-Ecosystems in East Asia and Assessment of its Environmental Impact*, 2004; pp 45−55.
108. Ma, J.; Ma, E. D.; Xu, H.; Yagi, K.; Cai, Z. C. *Soil Biol. Biochem.* **2009**, *41* (5), 1022–1028.
109. Ding, A.; Willis, C. R.; Sass, R. L.; Fisher, F. M. *Global Biogeochem. Cycles* **1999**, *13* (4), 1045–1052.
110. Ali, M. A.; Lee, C. H.; Kim, S. Y.; Kim, P. J. *Waste Manage.* **2009**, *29* (10), 2759–2764.
111. Kara, E. E.; Ozdilek, H. G. *Ekoloji* **2010**, *19* (74), 1–9.
112. Li, X. L.; Zhang, X. Y.; Xu, H.; Cai, Z. C.; Yagi, K. *Nutri. Cycl. Agroecosys.* **2009**, *85* (1), 31–40.
113. Zhan, M.; Cao, C. G.; Wang, J. P.; Jiang, Y.; Cai, M. L.; Yue, L. X.; Shahrear, A. *Nutri. Cycl. Agroecosys.* **2011**, *89* (1), 1–13.
114. Zheng, X.; Han, S.; Huang, Y.; Wang, Y.; Wang, M. *Global Biogeochem. Cycl.* **2004**, *18* (2), doi:10.1029/2003GB002167.
115. Cai, Z.; Laughlin, R. J.; Stevens, R. J. *Chemosphere* **2001**, *42* (2), 113–121.
116. Lu, Y. Y.; Huang, Y.; Zou, J. W.; Zheng, X. H. *Chemosphere* **2006**, *65* (11), 1915–1924.
117. Zou, J. W.; Huang, Y.; Zheng, X. H.; Wang, Y. S. *Atmos. Environ.* **2007**, *41* (37), 8030–8042.
118. Akiyama, H.; Yan, X. Y.; Yagi, K. *Global Change Biol.* **2010**, *16* (6), 1837–1846.
119. Jiang, J. Y.; Hu, Z. H.; Sun, W. J.; Huang, Y. *Agri. Ecosyst Environ.* **2010**, *135* (3), 216–225.
120. Rui, W. Y.; Zhang, W. J. Effect size and duration of recommended management practices on carbon sequestration in paddy field in Yangtze Delta Plain of China: A meta-analysis. Agriculture Ecosystems & Environment. *Agric. Ecosyst. Environ.* **2010**, *135* (3), 199–205.
121. Schlesinger, W. H. *Global Change Biol.* **2010**, *16* (2), 849–850.
122. Yan, X. Y.; Ohara, T.; Akimoto, H. *Atmos. Environ.* **2006**, *40* (27), 5262–5273.
123. Lu, F.; Wang, X. K.; Han, B.; Ouyang, Z. Y.; Zheng, H. *Chin. J. Appl. Ecol.* **2010**, *21* (1), 99−108. (In Chinese with English abstract).

124. Chen, H. Q.; Hou, R. X.; Gong, Y. S.; Li, H. W.; Fan, M. S.; Kuzyakov, Y. *Soil Tillage Res.* **2009**, *106* (1), 85–94.

125. Dong, W. X.; Hu, C. S.; Chen, S. Y.; Zhang, Y. M. *Nutri. Cycl. Agroecosys.* **2009**, *83* (1), 27–37.

126. He, J.; Kuhn, N. J.; Zhang, X. M.; Zhang, X. R.; Li, H. W. *Soil Use Manage.* **2009**, *25* (2), 201–209.

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

Chapter 7

Redox Potential Control on Cumulative Global Warming Potentials from Irrigated Rice Fields

Kewei Yu*

Department of Biological and Environmental Sciences,
Troy University, Troy, AL 36082
***E-mail: kyu@troy.edu**

Rice cultivation shifts between aerobic and anaerobic environment, making it a potential CH_4 source during flooding and a N_2O source during drainage. A favorable redox "window" of +180 to –150 mV was found where both N_2O and CH_4 productions were low. The trade-off emissions of CH_4 and N_2O found in rice field can be minimized by manipulating the soil profile through proper irrigation and drainage to maintain a favorable redox distribution. Various soil redox active components can effectively buffer the soil Eh change, in which Iron (Fe) probably plays a critical role. Development of best management practice in irrigated rice fields to mitigate greenhouse gas (GHG) emissions should consider reaching an overall minimum cumulative global warming potential (GWP) from CH_4 and N_2O emissions but not decreasing rice yield.

Introduction

Rice (*Oryza sativa*) is the most important food for more than half of the world's population. Rice cultivation area is about 155 million ha, making flooded rice (paddy) fields the largest man-made wetlands on earth. World rice production in 2008 was approximately 661 million tons. More than 90% rice production is taking place in Asia, with China accounting for 30% of total world production, followed by India (22%), Indonesia (9%), and Bangladesh (7%) (*1*).

Next to carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are the most important atmospheric greenhouse gases (GHGs) contributing to the enhanced global greenhouse effect. In 2005, the CH_4 concentration in

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

the atmosphere reached 1774 ppb, more than double its pre-industrial level. Meanwhile the N_2O concentration reached 319 ppb, about 18% higher than its pre-industrial level (*2*). To compare the potential climate impact of the emissions of different greenhouse gases with CO_2, Intergovernmental Panel on Climate Change (IPCC) introduced a metric of Global Warming Potential (GWP). Using CO_2 as a reference gas, GWP compares the integrated radiative forcing of different greenhouse gases over a specified period (e.g., 100 years), and the results can be expressed as CO_2 equivalent. In a 100-year time horizon, 1 kg of CH_4 and N_2O have been determined to be equivalent to 25 and 298 kg of CO_2, respectively, in radiative forcing of the global greenhouse effect (*2*).

Overall, wetland rice fields contribute more than 1/4 to global anthropogenic CH_4 emission (*2*). Nitrogen fertilization and drainage practice in rice fields also provide opportunities for N_2O emission. Rice fields, as well as other agriculture fields, can play an important role in mitigation of production and emission of CH_4 and N_2O to reach a sustainable food production because of the accessibility of direct management of this ecosystem. This chapter discusses critical soil factors that control CH_4 and N_2O emissions from rice ecosystems and summarizes several studies that attempted to identifiy the optimum rice growth conditions that minimize GHG emissions and the overall global warming potential from rice cultivation.

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

Redox Window with Minimum GWP from Soils

Nitrous oxide can be produced from nitrification under aerobic conditions, and denitrification under moderately reducing conditions. Significant CH_4 production generally needs strictly reducing conditions. The intensity of soil reducing condition can be instrumentally measured as soil oxidation-reduction (redox, Eh) potential (*3*). In natural environments, redox potential (Eh) can vary from well oxidizing conditions (Eh up to +700 mV) to strictly reducing conditions (Eh down to -300 mV).

Most of the soil redox reactions occur in an Eh range where water (H_2O) is stable, and the reactions are sequentially initiated as predicted in theory of redox chemistry (Table I). After flooding, microbial reduction processes sequentially use O_2, NO_3^-, Mn(IV), Fe(III), SO_4^{2-} and CO_2 as electron acceptors as Eh decreases, accompanied by the emission of various trace gases.

Aerobic (high Eh) and anaerobic (low Eh) conditions may be dominant for a certain period in rice soils depending on irrigation and drainage practice, making rice fields a major source of CH_4 during the flooded season, and an important source of N_2O during the non-flooded season (*5–7*). Such a trade-off relationship between CH_4 and N_2O emission makes mitigation of cumulative GWP from rice fields a great challenge. To explore the optimum redox conditions where the cumulative GWP from soils reaches the minimum, Yu and Patrick (*3*) conducted a soil incubation study with eight paddy soils (Table II) using a homogenous soil microcosm equipped with automatic monitoring of soil Eh and pH (Figure 1) (*8*). The Eh and pH conditions of the soil microcosm were closely monitored and controlled. Gas samples of GHGs (CH_4, CO_2, and N_2O) were frequently taken,

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

whenever Eh in the microcosm system changed by more than 10 mV, to monitor the dynamics of gas production under different Eh conditions.

The studied rice soils showed a large variation in pH and Eh change during the incubation from aerobic to anaerobic conditions. However, productions of N_2O and CH_4 in the soils showed a quite similar pattern when they were plotted against Eh, even though their production rates varied significantly under the similar incubation conditions due to large variations in soil characteristics (Table II). Nitrous oxide production, probably from both nitrification and denitrification, began immediately after the incubation started, but was mostly produced in an Eh range of +400 to +200 mV. Only a small amount of N_2O was present when the Eh was below +180 mV, due to stronger reduction of N_2O to N_2 at lower Eh (*10*). The critical Eh value to initiate a significant CH_4 production was about –150 mV at neutral pH (*10*, *11*). Although significant CH_4 production occurred at different time of the incubation for each soil, for all soils it happened only when the soil Eh decreased below –150 mV. Thus, major CH_4 production occurred in a narrow Eh range of -150 to about –300 mV, and the production rate increased greatly with Eh decrease within this Eh range. The results delineated a wide Eh range where the cumulative GWP from N_2O and CH_4 emissions reached a minimum (Figure 2). In this Eh range, soils were reducing enough to favor complete denitrification with N_2 as end product, but were still oxidizing enough to inhibit significant methanogenesis. The Eh "window" with minimum GWP contribution slightly varied for each soil, but generally located between +180 and –150 mV at pH 7. Carbon dioxide production showed an exponential decrease with decrease of soil Eh during the incubation. This favorable "redox window" remains valid even when CO_2 emissions were considered for total cumulative GWP (*8*).

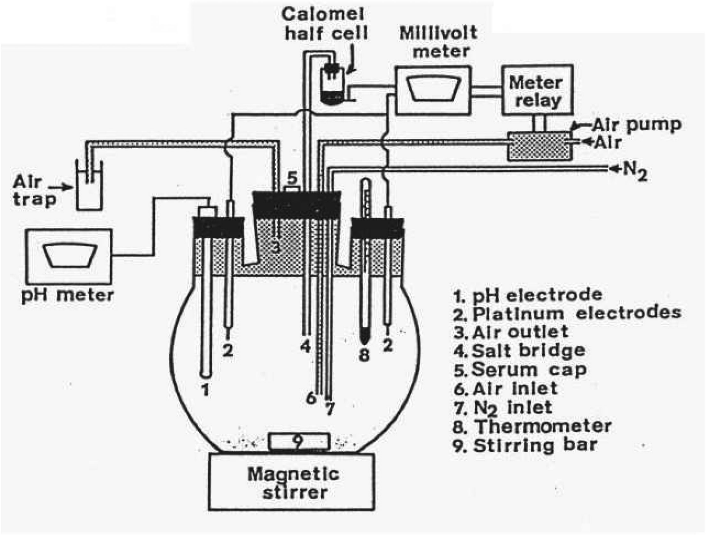


Figure 1. Soil microcosm system with redox and pH control ((9) with modification).

Table I. Redox potential of important reactions in soils (*4*)

Typical Reaction	*Standard Eh (mV)*
$O_2 + 4H^+ + 4e^- = 2H_2O$	1229
$2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O$	1240
$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1230
$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O$	1060
$SO_4^{2-} + 10H^+ + 8e^- = H_2S + 4H_2O$	300
$CO_2 + 8H^+ + 8e^- = CH_4 + 2H_2O$	170
$2H^+ + 2e^- = H_2$	0

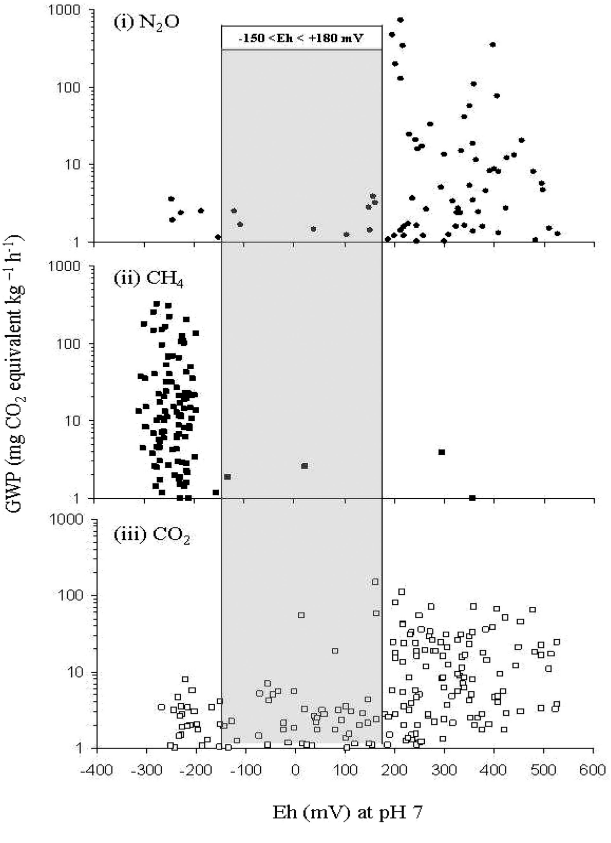


Figure 2. Soil Eh range with minimum GWP contribution ((8) with modification).

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

Table II. Selected characteristics of the sample soils

Soil	*pH*	*OM*	*Total N*	*Fe*	*Mn*	*S*
		mg kg^{-1}				
Arkansas	6.0	14.6	0.7	134	105	13
California	6.7	40.8	1.6	224	107	45
Louisiana	7.3	16.7	0.7	68	19	11
Mississippi	7.7	25.3	1.0	71	9	12
Texas	5.1	25.4	1.1	115	35	38
China	5.6	46.4	2.7	190	102	66
Indonesia	5.3	23.7	1.0	211	280	65
Thailand	4.7	25.8	1.2	173	40	190

Relative contributions of N_2O and CH_4 in the cumulative GWP at different Eh range were highly variable for each soil. On average of the eight soils, 57% of the total GWP was produced when Eh was higher than +180 mV, and 38% when Eh lower than -150 mV. Only 5% of the total GWP was produced in the Eh range of +180 to –150 mV that accounted for about 40% of the entire Eh range studied (*8*).

In a separate experiment using the same system, the Louisiana rice soil was incubated at different pH conditions (pH = 5.5, 7.0 and 8.5). The favorable Eh range with minimum N_2O and CH_4 production shifted to lower values of the Eh scale when pH increased as predicted by the Nernst equation (*12*). All above experiments were conducted from oxidizing to reducing conditions (an analog of flooding in rice fields). An incubation from reducing to oxidizing conditions (an analog of drainage in rice fields) was conducted using six of the above eight soils, resulting in the same conclusion on the favorable redox window with minimum N_2O and CH_4 emissions (*13*).

Drainage and Role of Iron (Fe) on CH_4 and N_2O Emissions

Early field-scale studies have observed the trade-off relationship between CH_4 and N_2O emissions during flooding periods and drainage periods (*5*, *6*, *14*). Redox potential oscillations due to rice field management control microbial community structure and function for various biogeochemical processes. The laboratory microcosm studies provide some guidelines for an optimistic perspective in mitigating GWP in rice soils if the soils could be maintained in this favorable redox range.

Mid-season drainage has been shown the most effective approach to reduce CH_4 emission from flooded rice fields, but with a potentially adverse effect of stimulating higher N_2O emission (*14*, *15*). Following the guidance of an optimum redox range with minimum CH_4 and N_2O productions, Johnson-Beebout and Olivyn (*16*) conducted a soil pot study was conducted to explore the possibility

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

of maintaining a “healthy redox” to reach simultaneous reduction of GWP from CH_4 and N_2O emissions in soil by irrigation/drainage control. The experimental pots contained soil without rice plant, and the Eh measurements were used to determine various irrigation schedules for different treatments. Surprisingly, the results found that more CH_4 emissions were found in two treatments with drainage/flooding cycle than in corresponding continuous flooding treatment. Unlike in rice fields where most of CH_4 emission is through rice plant (*17*, *18*), in soil pots the only pathway for CH_4 emissions is through soil/water surface. Consequently, less CH_4 surface emission from the continuous flooding treatment resulted in higher CH_4 concentration in the soil solution. On the other hand, drainage/flooding cycle facilitated CH_4 surface emission with less CH_4 dissolved in the soil solution (*16*). Due to heterogeneity of soil pots/fields conditions, interpretation of Eh measurements and gas emissions deserves careful attention. In soil microcosm studies, soils are in homogeneous slurry conditions where Eh measurements reflect the actual redox status of the system and all gases of interest are in equilibrium between headspace and soil slurry. Large Eh gradients exist in soil aggregates under natural conditions with aerobic (high Eh) outer layers and anaerobic (low Eh) inner layers (*19*). Frequent drainage/flooding cycle in soil pots/fields can significantly alter soil hydrological conditions that ultimately enhance gas release to the atmosphere by physical disturbance.

At a drainage event, atmospheric O_2 will enter soil pore space resulting in re-oxidation of various reduced redox active compounds in soils (*20*, *21*). Next to O_2 in soil pore space, Iron (Fe) could be the most important oxidant (electron acceptors) in rice fields. As seen in Table II, most of the soils have higher Fe content than that of Mn or S. The redox couple of Fe(III)/Fe(II) plays an important role in buffering redox status of rice fields (*22*). Methanogenesis can be controlled by inhibition due to the presence of O_2, and by competition for substrates (electron donors) due to the presence of alternative electron acceptors (*23*).

It has been observed that higher total Fe contents were found in paddy soils compared to in non-paddy soils (*24*, *25*). Thompson et al. (*26*) observed an increasing crystallinity of iron oxides during soil redox alternation (200–700 mV) in short-term batch experiments, which could be one of the reasons for the paddy soils to retain Fe. The critical Eh value for Fe(III)/Fe(II) conversion is about 100 mV at pH 7 (*27*). When Eh falls below 100 mV, Fe reduction and consequent dissolution occurs. Iron oxidation and immobilization occurs when Eh reaches higher than 100 mV.

Reducible Fe plays an important role to regulate soil redox status, and thus production and emission of both CH_4 and N_2O. Huang and Yu (*28*) studied the role of amendment of reducible Fe in soil on efficacy of drainage-based management to mitigate CH_4 emissions in a soil plot experiment. The results show that drainage, single or double, could greatly reduce CH_4 emissions, especially in Fe-amended treatments (Figure ()). In this study, Fe amendment showed no significant effect on rice yield ($p > 0.05$). Similar results were found in a study without continuous flooding (*29*). In a clay loam soil with original Fe content 3.9 g kg^{-1}, $Fe(OH)_3$ amendment by 3.3 g kg^{-1} reduced the cumulative CH_4 emission by 52%. Similar study conducted by Jäckel et al. (*30*) showed that ferrihydrite amendment 1046 g

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

m^{-2} reduced CH_4 emission by 50% in a sandy loam soil with original Fe content 2.5 g kg^{-1}.

The presence of Fe(III) can significantly delay the initiation of methanogenesis. The threshold concentration for H_2 and acetate utilization (two major CH_4 production pathways) by Fe(III) reducing bacteria is lower than that for methanogens (*31*). Exposure of soils to O_2 by temporal drainage allows regeneration of Fe(III) from its reduced form Fe(II). Therefore, the above inhibition of Fe(III) reduction on methanogenesis resumes. Aeration could result in higher CO_2 and N_2O production in general. However, proper management of drainage can minimize such increase. A case study by Ratering and Conrad (*32*) showed that the increase of CO_2 and N_2O production were <10% of the decreased production of CH_4, and did not represent a trade-off in terms of CO_2 equivalent.

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

Integration of Rice Yield and Reducing GWP from Rice Fields

Flooding a field for rice cultivation greatly limits the O_2 supply from the atmosphere, the microbial activities switch from aerobic (i.e. oxic condition) to facultative (i.e. hypoxic condition) and to anaerobic (i.e. anoxic condition) fermentation of organic matter, where alternative electron acceptors, such as Mn(IV) and Fe(III), are used. In such submerged soils, rice plants form aerenchyma that can enable the transport of atmospheric O_2 to the roots (*21*). Thus there exist two aerobic/anaerobic interfaces with large Eh gradients in rice ecosystem, water/soil interface and plant rhizosphere/bulk soil interface (*20*).

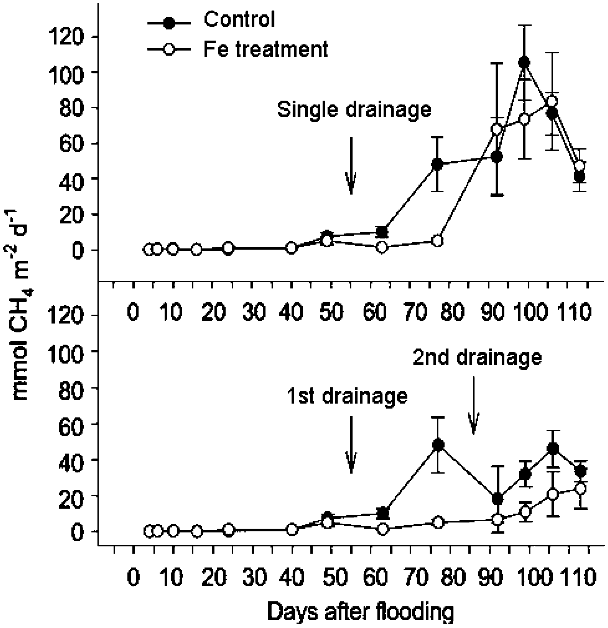


Figure 3. Methane emission (mean ± SD, n = 3) from cultivated rice. The arrows indicate the 2-day drainage ((28) with modification).

The different Eh conditions required for N_2O and CH_4 formation and the trade-off pattern of their emissions as found in above laboratory and pot experiments make it a great challenge to abate the production of one gas but not enhance the production of the other. Irrigation and drainage management can induce temporal and spatial variations in soil redox conditions that affect not only trace gas emissions but also rice yield. Thus, to propose feasible mitigation approaches, both cumulative GWP from N_2O and CH_4 emissions and rice yield need to be considered simultaneously.

In a field study conducted at Shenyang, China (41°32’ N, 122°23’ E) by Yu and Chen (*33*), effects of soil management on soil redox potential, GHG emissions, as well as rice yield were investigated. The soil had an OM content of 2.12% and 1.51%, respectively, for the field with and without annual application of organic manure (*6*). A major regional cultivar of rice was used for the study with a single growing season of about 120 days, during which three ammonium based nitrogen fertilizer applications were made, with a total N application rate of 170 kg N ha-1. The fields were kept under flooded and non-flooded conditions. The four treatments were: (A) No OM addition, flooded, (B) No OM addition, non-flooded, (C) OM addition, flooded, and (D) OM addition, non-flooded. The flooded fields kept 5 to 10 cm standing water, while the soil surface in the non-flooded fields was wet with water table fluctuating between the soil surface to approximately 5 cm below ground. The non-flooded treatments prevent great fluctuations of soil redox conditions as in conventional flooding/drainage cycle. Soil Eh was measured at depths of 1, 2, 4, 8, 14, and 22 cm below the soil surface. CH_4 and N_2O emissions in the rice field were measured at least once a week using a static chamber technique. Detailed experimental methodology is provided by Yu and Chen (*33*).

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

Effect of Field Management on Soil Redox Status

The variation of soil Eh in the rice fields is shown in Figure 4. Values of the measured Eh generally spanned a range of +700 to –300 mV. Unlike homogeneous soil suspensions used in a previous study by Yu and Patrick (*8*), both oxidizing and reducing conditions existed simultaneously in the rice fields, due to the heterogeneous nature of the field. Soil redox status under the different treatments showed a similar seasonal pattern (Figure 4). Flooding the field (A and C) and adding OM (C and D) facilitated the development of reducing conditions in the soils. After drainage, soil Eh in the upper layers of the field increased up to +450 mV in just a few days. Strictly reducing conditions (Eh < -150 mV) that were favorable for methanogenesis generally developed at 3 periods after rice transplanting: day 50 to 60 (early), day 67 to 77 (middle), and day 95 to 105 (late). Non-flooding conditions (B and D) provided more aeration to the top layers of the fields than the flooded fields (A and C), and consequently resulted in the strictly reducing zones (Eh < -150 mV) being developed 4 or 5 cm deeper than in the flooded fields.

Irrigation and OM management practice showed a significant impact on the soil redox status. Under the flooding conditions, the bulk soil with Eh < 0 mV accounted for 63 and 50% of the soil (top 22 cm) with (treatment C) and without (treatment A) OM addition, respectively. The non-flooding management enlarged the volume of bulk soil with higher Eh, and in compensation reduced the portion of soil with lower Eh (Figure 4 and Figure 5). The lower water table in the treatment B and D aerated the soil surface layers, thus strictly reducing conditions developed at deeper layers of the soil profile where reducing intensity was strong enough to initiate a significant CH_4 production.

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

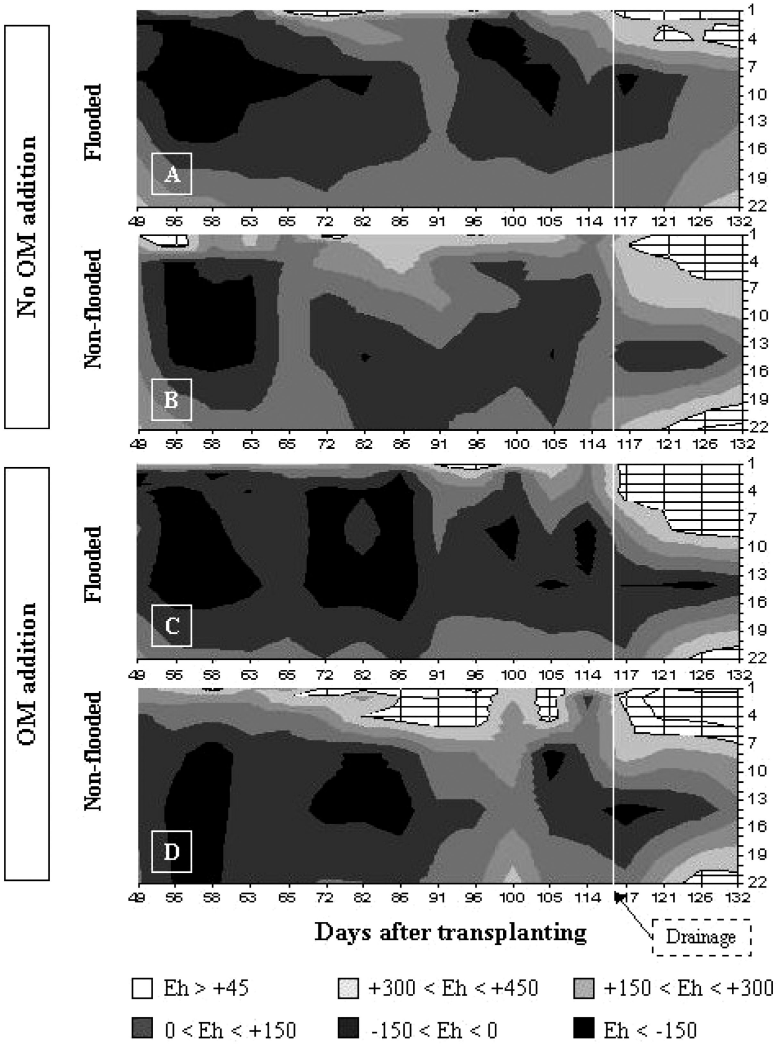


Figure 4. Soil Eh profile under different treatments ((33) with modification). Treatment: (A) No OM addition, flooded; (B) No OM addition, non-flooded; (C) OM addition, flooded; (D) OM addition, non-flooded.

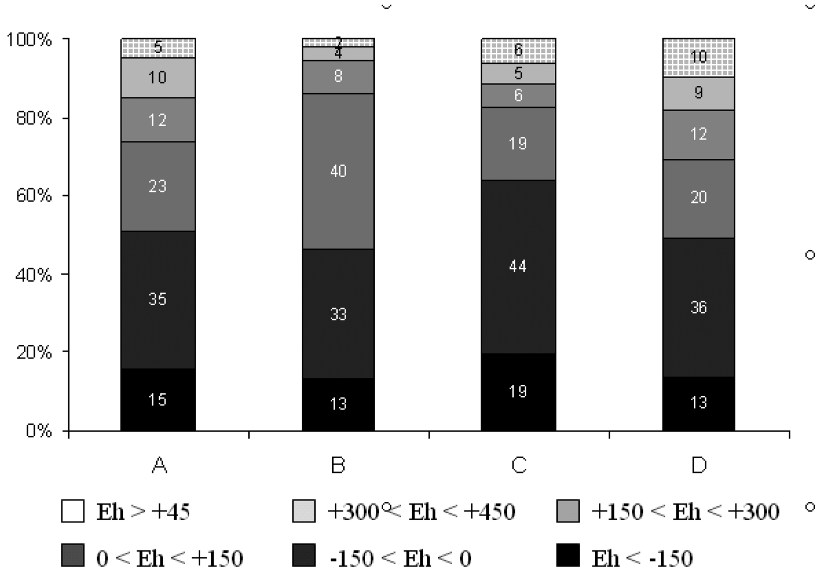


Figure 5. Relative portion of the soil volume at each Eh range ((33) with modification). Treatment: (A) No OM addition, flooded; (B) No OM addition, non-flooded; (C) OM addition, flooded; (D) OM addition, non-flooded.

Methane production mostly occurs in soil microenvironments where the Eh values are lower than what is normally measured (*34*). However, soil Eh measurement can qualitatively indicate the redox status in the soil microenvironment, especially in flooded soils where soil aggregates tend to break down. When measured soil Eh is lower, the soil microenvironment is more reducing, and vice versa (*19*). Soil OM is the major electron donor in various soil redox reactions, and is the driving force of developing soil-reducing conditions. Release of new OM from the rice root and degradation of the dead rice roots significantly contributed to developing the middle and late strictly reducing zones, respectively (*35*). In the fields without receiving OM where the rice was in poor growth (with less rice yield, see Table III), less reducing zones developed in the middle season, probably due to less root exudates or dead root tissues from the rice plants. Oxygen diffusion through the rice plant might play a significant role in elevating the soil Eh level between the three strictly reducing periods of the soils.

Effects of Field Management on CH_4 and N_2O Emission, and on Rice Yield

Major periods with higher CH_4 and N_2O emission generally remained the same among the different treatments (Figure 6), which also agreed quite well with the previous measurements in the same rice field where more complete seasonal variations of CH_4 and N_2O emission were recorded (*6*). The three periods with major CH_4 emission in the rice fields corresponded to the seasonal development of the strictly reducing conditions in the soils (Figure 6), indicating a close relationship between soil Eh and methanogenesis activity. The highest CH_4

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

emission was found in the treatment C (OM addition, flooded), and the lowest in the treatment B (No OM addition, non-flooded). Flooded fields showed low N_2O emission, and occasional consumption of ambient N_2O. Nitrogen fertilization during the rice-growing season stimulated higher N_2O emission, especially in the non-flooded fields (Figure 6). Drainage at the end of the season also resulted in higher N_2O emission, but meanwhile terminated CH_4 emission in the fields.

Table III summarizes major results of this field study. When the rice fields were flooded, no addition of OM reduced the CH_4 emission by 57% with no difference in average N_2O emission. Without OM addition, non-flooding management reduced the cumulative GWP from both CH_4 and N_2O by 46%, but about one third of the CH_4 emission reduction (176.6 CO_2 equivalent m^{-2} d^{-1}) was offset by the increase of N_2O emission (56.2 CO_2 equivalent m^{-2} d^{-1}). In the OM added fields, non-flooding management reduced the cumulative GWP by 72% as a result of the CH_4 emission reduction by 458.2 CO_2 equivalents m^{-2} d^{-1}, and the N_2O emission increase by 29.6 CO_2 equivalents m^{-2} d^{-1}. Although the local traditional management (treatment C) showed the highest GWP, appropriate irrigation (e.g., treatment D) could effectively reduce the cumulative GWP by a significant reduction of CH_4 emission with little enhancing N_2O emission from the rice field. More O_2 was available for the soils under the non-flooding conditions, thus a larger portion of the soil OM converted to CO_2, instead of converting to CH_4 by methanogenesis under the strictly anaerobic conditions.

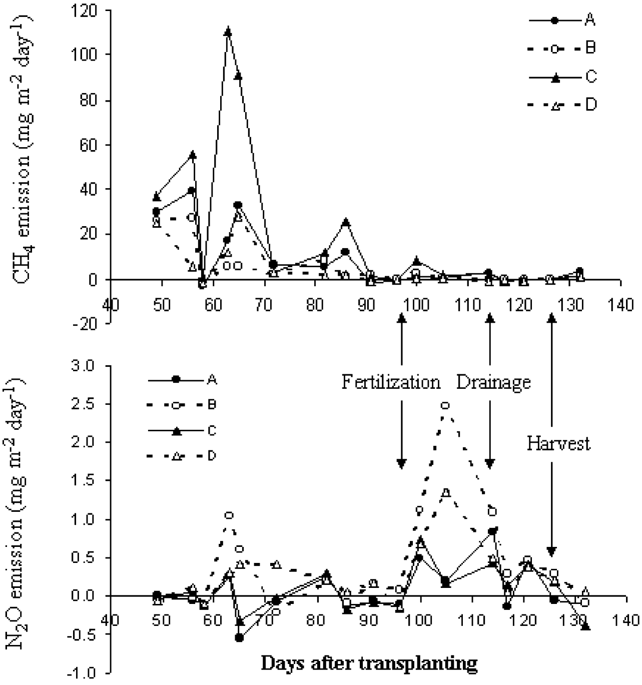


Figure 6. Seasonal CH_4 and N_2O emissions in the rice fields ((33) with modification). Treatment: (A) No OM addition, flooded; (B) No OM addition, non-flooded; (C) OM addition, flooded; (D) OM addition, non-flooded.

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

Table III. Summary of the rice field study results ((*33*) with modification)

Measurement	*Treatment*			
	A	*B*	*C*	*D*
CH_4 (mg m^{-2} d^{-1})	10.80 (95)	3.12 (51)	25.20 (98)	5.28(75)
N_2O (mg m^{-2} d^{-1})	0.04 (5)	0.23 (49)	0.04 (2)	0.14(25)
GWP (mg m^{-2} d^{-1})	260	140	591	163
Yield (ton ha^{-1})	9.7	8.8	11.5	10.9

(A) No OM addition, flooded; (B) No OM addition, non-flooded; (C) OM addition, flooded; (D) OM addition, non-flooded. Data in parenthesis denotes the relative contribution (%) of CH_4 or N_2O in the cumulative GWP.

Soil OM played an important role in rice yield (Table III). When additional OM was provided, rice plants showed a more healthy growth as observed in the field and higher yield at harvest regardless of irrigation conditions. This was probably due to the additional nutrients (e.g., phosphorus) in the organic manure and a generally beneficial effect of OM on soil fertility. Compared with the local traditional management (treatment C), the rice yield was significantly decreased ($P < 0.05$) by 16% if no additional OM was applied (treatment A), and by another 9% if the field was non-flooded (treatment B). Therefore, addition of OM should be included in the field management practice, at least for this region, because of the top priority for higher rice yield. Non-flooded management didn't show any water stress to the rice plant growth, and the rice yield was not decreased in this field trial. With OM addition, non-flooding treatment (D) showed no significant ($P > 0.05$) reduction in rice yield (5%).

The wide Eh range (+180 to –150 mV) with minimum N_2O and CH_4 production found in the laboratory studies can be used to guide field management to achieve a maximum reduction of cumulative GWP from CH_4 and N_2O in rice fields. Although soil Eh in entire soil profile of the rice fields cannot be regulated within such an Eh range, proper irrigation management can make the soil Eh distribute in a desirable way to largely reduce CH_4 emission with little enhancing N_2O emission.

Irrigation and drainage showed a critical impact on controlling the soil redox status, and on CH_4 and N_2O production and emission. The best management practice proposed in this field study, in order to reduce the cumulative GWP from the rice field without decreasing the rice yield, is to keep the field non-flooded with OM addition (treatment D). This is a minor modification of the current local management practice (treatment C), which would make it more feasible in application. Less water used for the non-flooded fields may provide some additional benefits to the farmers with less labor, water, and electricity expenses. This management approach may also be feasible for the rice fields with no information available on seasonal variation of CH_4 and N_2O emission, because irrigation control is adjusted according to the wetness of the soil surface, instead of any instrumental measurement.

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

Increasing N_2O production and emission can significantly offset CH_4 reduction during the drainage or non-flooded practice in mitigating CH_4 emission, resulting in low efficacy in overall GWP reduction. However, higher N_2O production and emission is always associated with N-fertilization during the rice-growing season. The results also suggest a possible modification to the currently proposed management practice (treatment D) to reduce the short-term higher N_2O emission by temporarily flooding the fields upon fertilization (only applied to ammonium-based fertilizers). Such temporary flooding condition may prevent the undesirable nitrification activity that makes the fertilizer N unstable, and limits N_2O production and emission as found under the flooding conditions (Figure 6, and Table III). This modification will not affect the feasibility of the proposed field management, but how long the field should be flooded after fertilization, without introducing significant CH_4 emission, deserves further investigation.

Conclusion

Mitigating GHG emission from agricultural ecosystem is a promising approach to abate the current global climate change, because this ecosystem is under direct human management. The theoretical redox window with minimum cumulative GWP emission from soils provides an important guidance in irrigation and fertilization management of rice field. Due to the heterogeneous nature of rice field, Eh measurement and critical Eh condition for CH_4 and N_2O emission should be carefully interpreted. Irrigation control should minimize significant methanogenesis and nitrification, while favoring complete denitrification with N_2 as the end product. Timing and duration of drainage should be field specific, depending on the soil Eh buffering capacity. All management practice should consider rice yield as a high priority. Significant reduction of GWP by proper management will greatly compensate the projected higher GHG emissions from rice fields due to demand increase by growing population, which will make the rice ecosystem environmentally sustainable.

References

1. Internal Rice Research Institute (IRRI), **2010**, URL http://beta.irri.org/statistics.
2. Intergovernmental Panel on Climate Change (IPCC), Technical Summary. In *Climate Change 2007*; Cambridge University Press: New York, 2007
3. Bohn, H. L. *Soil Sci.* **1971**, *112*, 39–45.
4. Lide D. R. In *Handbook of Chemistry and Physics*, 72nd ed.; CRC Press: Boca Raton, FL, 1991.
5. Cai, Z. C.; Xing, G. X. *Plant Soil* **1997**, *196*, 7–14.
6. Chen, G. X.; Huang, G. H. *Nutr. Cycling Agroecosyst.* **1997**, *49*, 41–45.
7. Tsuruta, H.; Kanda, K. *Nutr. Cycling Agroecosyst.* **1997**, *49*, 51–58.
8. Yu, K. W.; Patrick, W. H. *Soil Sci. Soc. Am. J.* **2004**, *68*, 2086–2091.
9. Patrick, W. H.; Williams, B. G. *Soil Sci. Soc. Am. Proc.* **1973**, *37*, 331–332.

10. Masscheleyn, P. H.; DeLaune, R. D. *Chemosphere* **1993**, *26*, 251–260.
11. Wang, Z. P.; Delaune, R. D. *Soil Sci. Soc. Am. J.* **1993**, *57*, 382–385.
12. Yu, K. W.; Patrick, W. H. *Soil Sci. Soc. Am. J.* **2003**, *67*, 1952–1958.
13. Yu, K. W.; Böhme, F. *Soil Sci. Soc. Am. J.* **2007**, *71*, 1406–1417.
14. Bronson, K. F.; Neue, H. U. *Soil Sci. Soc. Am. J.* **1997**, *61*, 981–987.
15. Wassmann, R.; Lantin, R. S. *Nutr. Cycling Agroecosyst.* **2000**, *58*, 23–36.
16. Johnson-Beebout, S. E.; Olivyn, R. A. *Geoderma* **2009**, *149*, 45–53.
17. Yu, K. W.; Wang, Z. P. *Biol. Fert. Soils* **1997**, *24*, 341–343.
18. Sass, R. L.; Fisher, F. M. *Global Biogeochem. Cycles* **1990**, *4*, 47–68.
19. Tiedje, J. M.; Sexstone, A. J. *Plant Soil* **1984**, *76*, 197–212.
20. Reddy, K. R.; Patrick, W. H. *Limnol. Oceanogr.* **1989**, *34*, 1004–1013.
21. Begg, M. B.; Kirk, G. D. *New Phytol.* **1994**, *128*, 469–477.
22. Yao, H.; Conrad, R. *Biogeochemistry* **1999**, *47*, 269–295.
23. Kimura, M.; Murakami, H. *Soil Sci. Plant Nutr.* **1991**, *37*, 55–60.
24. Zhang, G. L.; Gong, Z. T. *Geoderma* **2003**, *115*, 15–29.
25. Cheng, Y. Q.; Yang, L. Z. *Geoderma* **2009**, *151*, 31–41.
26. Thompson, A.; Chadwick, O. A. *Geochim. Cosmochim. Acta* **2006**, *70*, 1710–1727.
27. Patrick, W. H.; Jugsujinda, A. *Soil Sci. Soc. Am. J.* **1992**, *56*, 1071–1073.
28. Huang, B.; Yu, K. W. *Chemosphere* **2009**, *74*, 481–486.
29. Watanabe, A.; Kimura, M. *Commun. Soil Sci. Plant Anal.* **1999**, *30*, 2449–2463.
30. Jäckel, U.; Russo, S. *Soil Biol. Biochem.* **2005**, *37*, 2150–2154.
31. Lovley, D. R.; Phillips, E. J. *Appl. Environ. Microbiol.* **1989**, *55*, 700–706.
32. Ratering, S.; Conrad, R. *Global Change Biol.* **1998**, *4*, 397–407.
33. Yu, K. W.; Chen, G. X. *Global Biogeochem. Cycles*, 2004, *18*, GB3018, doi:10.1029/2004GB002251.
34. Neue, H. U. *Soil Use Manage.* **1997**, *13*, 258–267.
35. Schutz, H.; Seiler, W. *Biogeochemistry* **1989**, *7*, 33–53.

Downloaded by STANFORD UNIV GREEN LIBR on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch007

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

Chapter 8

Fertilizer Nitrogen Management To Reduce Nitrous Oxide Emissions in the U.S.

Robert L. Mikkelsen* **and Clifford S. Snyder**

International Plant Nutrition Institute, 3500 Parkway Lane, Suite 550,
Norcross, GA 30092, U.S.A.
***E-mail: rmikkelsen@ipni.net**

Food, fiber, and fuel demands of a growing global population are resulting in increased fertilizer nitrogen use. Correct N management decisions, based on agronomic and environmental research, can improve crop production and help reduce GHG emissions. Residual soil nitrate and emissions of N_2O may be minimized when best management practices for fertilizer N are implemented. Balanced fertilization with other essential nutrients also enhances N use efficiency. Emissions of N_2O vary among fertilizer N sources, depending on cropping conditions. With intensive crop management, GHG emissions are not necessarily increased per unit of production. Such ecological intensification of crop production can help spare natural areas from conversion to cropland and preserve lands for GHG mitigation. Use of the right source, at the right rate, right time, and right place - termed 4R Nutrient Stewardship - is advocated, in combination with appropriate cropping and tillage practices, to achieve agronomic, economic, and environmental goals.

The three principal biogenic greenhouse gases (GHGs) which contribute to global warming and climate change are: carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4). Atmospheric concentrations of these GHGs have increased greatly since the 18th century as a result of human activities.

These GHG emissions have been associated with global average temperature increases of 0.6 °C (1 °F) in the 20th century and it has been projected that temperatures may increase 2 to 6 °C (3.6 to 10.8°F) during the 21st century (*1*). In addition to these temperature changes, GHG effects on climate change may result in altered precipitation patterns, sea level rise, and other changes in physical and hydrological systems (*2*).

Greenhouse Gas Emissions and Agriculture's Contributions

The global increases in atmospheric CO_2 are primarily due to fossil fuel use and land use changes. Increases in atmospheric N_2O and CH_4 are attributed primarily to agriculture (*3*). According to Le Quéré et al. (*4*), the current growth in CO_2 emissions is closely linked to the growth in the world gross domestic product. It was estimated that agricultural production accounted for 10 to 12% of the total global GHG emissions in 2005 (5.09-6.19 Gt of CO_2). Flynn and Smith (*5*) reported that approximately 60% of the global total N_2O emissions and 50% of the global CH_4 emissions are attributed to agriculture. Land use change, associated with the clearing of forests and the conversion of native lands for agricultural production, accounted for between 6 and 17% of the global total GHG emissions.

The radiative forcing potential of N_2O is 296 times greater than the radiative forcing potential of CO_2. Radiative forcing refers to the capacity of the molecule to trap long-wave infrared radiation. Relatively small amounts of N_2O emitted into the atmosphere will have a much greater effect on the ability of the atmosphere to trap heat than a similar amount of CO_2. Further N_2O has an atmospheric lifetime of 100 years or more. A molecule of N_2O emitted into the air today could persist for over a century. This chapter focuses on N_2O because of its high radiative forcing potential and its close linkage to agricultural practices.

Global fertilizer production and use has made it possible to provide 40 to 60% of the current global crop and food production (*6*, *7*). Although fertilizers have had a tremendously beneficial impact on society, the environmental consequences should also be considered. Based on the Intergovernmental Panel on Climate Change (*8*) the world's fertilizer N consumption caused the emission of 1.46 Mt of N_2O or about 433 Mt of CO_2 equivalent, approximately 7 to 9% of the global total GHG emissions in 2005 (*5*). Fertilizer N consumption in the U.S. has generally trended upward since the mid-1980s, and approached 12 million tonnes of N in the year ending June 30, 2007 (Figure 1). Agriculture contributes 6% of all U.S. GHGs (*9*), however agricultural soil management, which includes nitrogen fertilization, accounted for 68% of the N_2O emissions in the U.S. in 2008 (Figure 2).

There are many reasons for improving N fertilizer management. Fertilizer use has broad environmental, economic, and social implications, as well as a direct link with food. Fertilizers are estimated to be responsible for up to 50% of the current global food supply (*6*, *7*). With strategic agricultural intensification on existing crop land, massive deforestation and land clearing could be avoided (*10*). Agricultural intensification and appropriate N fertilizer use also is responsible for limiting GHG emissions, compared with low-yielding food production (*11*).

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

Cropping System Management

Interactions between cropping systems and specific management practices can directly affect GHG emissions by altering mineral N concentrations, or indirectly through impacts on the soil microclimate and effects on C and N cycling. Combined emissions of N_2 and N_2O (via denitrification) are usually greater in wetter soils, especially when the water-filled pore space exceeds 60% (*12*). Factors such as tillage practices, natural and artificial internal soil drainage, and winter cover crops may act independently or interactively to influence the frequency and duration of N_2O emissions, as well as the cumulative growing season emissions (*13*).

In a comparison of low input corn-soybean-wheat rotations with more intensively managed continuous corn or a corn-soybean rotation, Snyder et al. (*13*) found that the contrasting systems were rather comparable with respect to the global warming potential (GWP) per unit of food produced. However, the more intensively managed cropping systems produced more food per unit land area and were thus able to spare more natural lands (forest, wetlands, native grasslands) from agricultural production encroachment. This premise is supported with additional evidence by van Groenigen et al. (*14*) who stated that the true N_2O efficiency of a cropping system can be expressed by relating N_2O emissions per unit of above-ground N uptake or per unit of crop yield, and that "expressing N_2O emissions as a function of land area or fertilizer application rate is not helpful and may even be counterproductive". The goal of optimizing biological productivity must also be considered when restrictions on N_2O are considered.

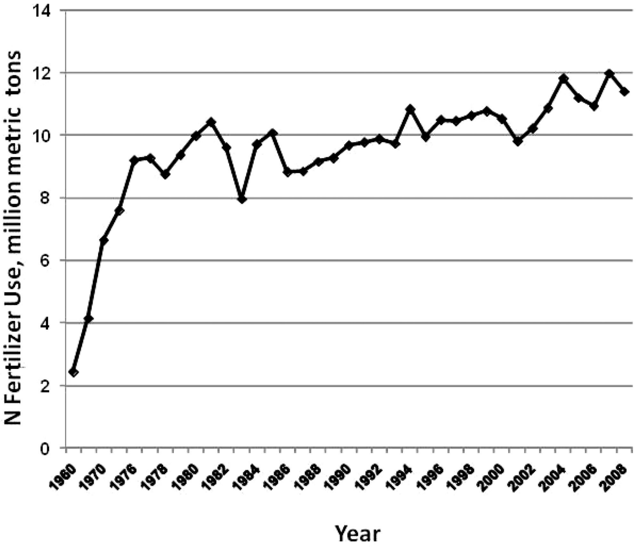


Figure 1. Annual consumption of fertilizer N in the U.S. (Source: Association of American Plant Food Control Officials and The Fertilizer Institute).

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

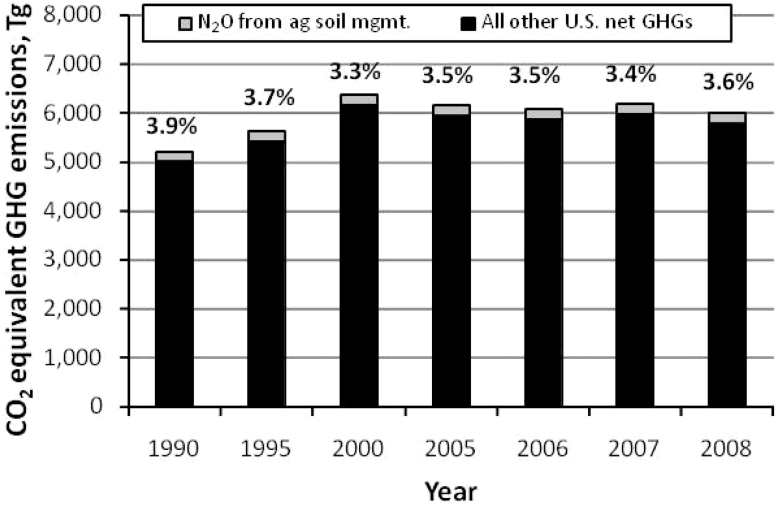


Figure 2. Trends in 1990-2008 total U.S. greenhouse gas (GHG) emissions, and portion of total GHG emissions attributed to nitrous oxide (N_2O) which are associated with agricultural soil management (9).

Fertilizer N Management and 4R Nutrient Stewardship

The International Plant Nutrition Institute (IPNI), The Fertilizer Institute (TFI), the Canadian Fertilizer Institute (CFI), and the International Fertilizer Industry Association (IFA) have advocated improved fertilizer management through a systematic 4R Nutrient Stewardship program (*use of the Right source at the Right rate, Right time and Right place*). This approach is designed to improve the efficiency and effectiveness of fertilizer use while simultaneously protecting the environment (e.g. (*15–17*)).

1. Right N Source

In a review of the effects of fertilizer N source, rate, timing, and placement on direct soil GHG emissions, Snyder et al. (*13*) reported a wide range in N_2O emissions from a given fertilizer N source, as well as among sources. It is clear that there is no one “right N source” that will minize N_2O emissions in all cropping conditions. For example, Bouwman et al. (*18*, *19*) reported that N_2O emissions were lower for nitrate-based fertilizers compared to organic, organic-synthetic, or ammonium-based fertilizers. However under different soil conditions Stehfest and Bouwman (*20*) showed that there was little difference in N_2O emissions among fertilizer N sources after accounting for crop species, climate, soil organic carbon, soil pH, duration of the growing season, and the rate of fertilizer application.

One might anticipate higher N_2O loss when nitrate-N is abundant in soil systems, since NO_3^- and NO_2^- are essential for denitrification, although some quantity of N_2O can also be emitted during nitrification (*21*, *22*). Harrison and Webb (*23*) reported that relative N_2O emissions from nitrate-based fertilizer

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

sources may be greater than those from ammonium-based sources, and that differences between sources may be greater with increasing soil wetness. Chen et al. (*24*) stated, “Since ammonia or ammonium-producing compounds are the main sources of fertilizer N, maintenance of the applied N in the ammoniacal form should result in lowered emissions of nitrous oxide from soils”. However, higher N_2O emissions with anhydrous ammonia compared to other N sources has been observed in several studies (*25–27*). Higher N_2O emissions with ammonium-based fertilizers may be related to potential nitrite (NO_2^-) accumulation or N_2O production during nitrification (*28*). In contrast, no differences in N_2O emissions between anhydrous ammonia and urea were found by Burton et al. (*29*) in Manitoba, Canada. It is possible that fertilizer source effects on N_2O emissions may be less important than the size of the mineral N pool, and soil conditions conducive to rapid nitrification and denitrification. Mosier et al. (*30*) considered soil management and cropping systems to have a greater impact on N_2O emissions than mineral N source.

More recent evidence in the U.S. has shown that in certain environments, the proper selection of N source can significantly reduce N_2O emissions. Venterea et al. (*27*) observed 50% lower emissions with urea compared to anhydrous ammonia applied in the spring for corn in Minnesota. Hyatt et al. (*31*) observed 39% lower emissions with a single pre-plant polymer-coated urea application versus conventional split applications of urea and ammonium nitrate in potato production in Minnesota. When comparing enhanced efficiency fertilizers (EEFs) with traditional N fertilizers in an irrigated no-till corn study in Colorado, Halvorson et al. (*32*) found that EEFs significantly reduced cumulative N_2O emissions by up to 53% compared with commonly used urea. The EEFs were ESN and Duration III (polymer-coated urea fertilizers), and two N fertilizers containing nitrification and urease inhibitors (Super U and UAN + AgrotainPlus) (Figure 3).

The effects enhanced-efficiency fertilizers (EEF) with nitrification and/or urease inhibitors or various controlled-release fertilizers were recently reviewed by Snyder et al. (*13*), and will not be repeated in detail here. The potential benefit of EEF materials is largely through the control of the timing of N release and/or the supply of N in certain forms. These fertilizer characteristics can improve crop N recovery and potentially lessen environmental losses compared with traditional soluble N fertilizers. The use of new EEFs to improve crop N recovery and reduce environmental losses is an area of active research and scientific workshops.

Shaviv (*33*) and Chien et al. (*34*) reported that controlled-release fertilizer technologies have potential to reduce leaching losses of nitrate, reduce volatile losses of N as NH_3, and reduce N_2O emissions by affecting the timing of N release from fertilizer. Urease inhibitors can reduce ammonia volatilization losses and nitrification inhibitors can help reduce the potential for nitrate losses via leaching and denitrification. Reductions in these N losses may improve crop N recovery and provide greater stability in fertilizer N performance.

Use of a nitrification inhibitor (nitrapyrin) with fall-applied anhydrous ammonia did not reduce N_2O emissions over two years of rainfed corn production in Iowa (*35*). Use of EEFs (ESN, Super U, UAN + AgrotainPlus) did not significantly reduce N_2O emissions compared with UAN applications, and can

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

sometimes increase N_2O emissions (personal communication, Tim Parkin, USDA ARS, April 2010). In a review of the effectiveness of EEFs to mitigate N_2O and NO emissions from agricultural soils, Akiyama et al. (*36*) reported that fertilizer N with nitrification inhibitors and polymer coated urea fertilizers significantly reduced N_2O emissions compared to conventional N fertilizers (Table 1). The addition of a urease inhibitor to urea-containing fertilizer was not consistently effective in reducing N_2O losses, but they only considered a limited number of studies and only two inhibitors were evaluated (n-butyl thiophosphoric triamide and hydroquinone).

It is important to note that Akiyama et al. (*36*) made no attempt to standardize or partition the data by fertilizer N rates, methods of incorporation, or placement. Akiyama et al. (*36*) recognized limitations to their review of N sources which could qualify their findings. For example, fertilizer application rate, method, placement and timing may influence N_2O emissions (*18*, *37*, *38*). Also, the effects of polymer-coated fertilizers showed mixed results among land-use types and soils, with significant N_2O emission reductions in poorly drained soils but no reductions in well-drained upland soils.

2. Right N Rate

Improper accounting of residual nitrate in the root zone can result in increased soil nitrate accumulation and leaching losses, especially where precipitation and irrigation exceeds evapotranspiration. Nitrogen management to minimize the presence of excessive nitrate during periods when there is a high risk of denitrification (warm and wet) may help limit losses of N_2O. When other factors are held constant, increased fertilizer N rates considerably above the economic optimum N rate (EONR) may increase nitrate accumulation and the risk of N_2O emissions (*39*). It is well recognized that N rates considerably above the EONR can raise the risk of nitrate leaching and increase the risk of direct N_2O emissions and should be avoided (*14*, *38*).

Many environmental properties and management practices have a strong influence on biological processes, including nitrification and and denitrification. Nitrous oxide emissions do not always exhibit a strong linear correlation with increases in soil nitrate (*40*). The N_2O emissions may be affected more by the biological N transformations rather than the mineral N pool size per se, which is in agreement with Mosier et al. (*30*).

Measurement of residual nitrate and its calibration with crop response to additional N fertilizer has been attempted by many scientists, but the work has proven to be quite challenging because of large temporal and spatial variation, and the differences among agro-ecosystems. Successful nitrate measurement and N fertilizer calibration has been achieved in some regions, but wide ranges in crop response to residual nitrate or mineralizable N is common (*41*). Typically, there is a wide scatter of data points instead of a distinct calibration curve (*42*). Calibration of soil nitrate tests has generally been less successful in humid areas than in less humid areas. Nevertheless, where residual soil nitrate tests have been successfully calibrated through field research, they should be used as part of the comprehensive nutrient management plan to optimize crop response to N and minimize the potential for nitrate loss. Indirect loss of nitrate to water resources can lead to N_2O emissions off of the farm (*43*).

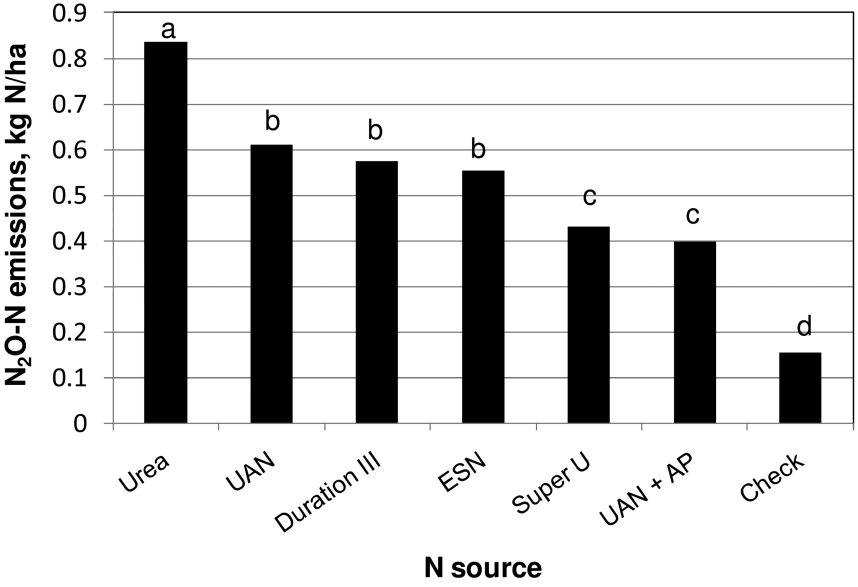


Figure 3. The effect of N fertilizer source on cumulative N_2O-N emissions averaged for the 2007 and 2008 growing seasons (32). (Sources with different letters above the bars are significantly different at α = 0.05 probability level).

Table 1. The effect of nitrification inhibitor-treated N fertilizer, polymer-coated N fertilizer, and urease inhibitor-treated N fertilizer on relative N_2O emissions in field experiments (*36*)

Mitigating fertilizer technology	***Number of observations (n)***	***Mean N_2O emission mitigation (%)***	***95% confidence interval (%)***
Nitrification inhibitor	85	-38*	-44 to -31
Polymer coating	20	-35*	-58 to -14
Urease inhibitor (NBPT)	6	+10^{NS}	-4 to +35

* Statistically significant reduction in N_2O emission compared to conventional N fertilizers. ^{NS} Not significantly different from conventional urea-containing fertilizers.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

3. Right N Time and Place

The interactive effects of time and place of N application with fertilizer source and application rate make it difficult to isolate individual management decisions. Bouwman et al. (*18*) indicated that N_2O emissions might be decreased by shortening the time in which ammonium-based fertilizers can undergo nitrification, or minimizing the time which nitrate-based fertilizers reside in the rootzone and are at risk for denitrification. Synchronizing the time of N application to coincide with plant physiological growth stages would be ideal. Such ideal timing is usually only economically and logistically practical under certain intensively managed fertigation systems. Uncertainty due to weather, unpredictable soil N release, labor constraints, and other management challenges cause many farmers to apply N in advance of when the plants need it in order to avoid agronomic and economic N deficiencies (*44*). On-the-go N–sensing technologies are being developed and calibrated for some major crops in the U.S. (corn, wheat, cotton) to adjust N fertilization practices to dynamic in-season crop demand (*45*, *46*).

Timing and placement of urea-containing N fertilizer to allow incorporation beneath crop residues and into the soil within a few days after application can help reduce ammonia volatilization losses, which can indirectly contribute to increased N_2O emissions (*43*, *47*) (since more N fertilizer is required to compensate for volatilized N). In drill-seeded rice culture in the southern U.S., Griggs et al. (*48*) reported that ammonia emissions can exceed 30% of the urea N applied if soil incorporation by field flooding does not occur within 14 days after the urea is broadcast on the surface.

It is generally assumed that the proportion of N emitted as N_2O is the same, whether the applied N stays available in the soil for crop uptake or it goes elsewhere as volatilized ammonia. For this reason, fertilizer N BMPs that reduce ammonia volatilization may also reduce N_2O emissions in the same proportion as the amount of N in the system is conserved. Hultgreen and Leduc (*49*) reported that when urea was placed in a band below and to the side of the seed-row, lower N_2O emissions resulted when compared to urea broadcast on the soil surface. In many small grain cropping systems, such as in Canada and the northern U.S., farmers commonly place N and P fertilizers beneath the soil surface to enhance crop nutrient recovery and to increase yields. Higher crop N recovery translates to improved N use efficiency and reduced risks of direct and indirect N_2O emissions.

Bouwman et al. (*18*) summarized data from over 800 studies and concluded that emissions of N_2O were lower with subsurface injection of N compared to surface broadcast applications. Unfortunately, in many studies the placement of N is confounded with source of N, making it difficult to make interpretations about optimal N placement depth to maximize crop N recovery. Shallow applications of ammonium nitrate to corn as a side-dress application 2-cm deep resulted in lower N_2O emissions compared to placement 10-cm deep in a study comparing tillage systems in Canada (*50*). Similarly, shallow injection (10 to 20 cm) of anhydrous ammonia in Iowa resulted in lower N_2O emissions than with deeper (30cm) injection, possibly by avoiding placement of N in a zone with higher soil moisture, elevated denitrification, and a heightened risk of N_2O loss (*51*). In contrast, Liu

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

et al. (*52*) found that shallow (5cm) placement of a fluid fertilizer containing urea ammonium nitrate in an irrigated no-till continuous corn production system in northeastern Colorado resulted in higher N_2O emissions compared to placement at a 10 or 15 cm depth. Clearly there many site-specific factors that need to be considered when selecting the most appropriate placement of N fertilizer.

Noellsch et al. (*53*) demonstrated that applications of different fertilizer N sources (including a polymer-coated urea) across undulating landscapes can result in improved crop N recovery and higher yields in some years, especially in the low-lying positions. Improved crop N recovery typically results in lower potential environmental losses of N, including lower N_2O emissions. We are not aware of similar variable-rate and variable-source N studies elsewhere, and would note that this is an area in need of further research attention.

It is clear that there is no “one size fits all” approach to N fertilizer management that can reduce emissions of N_2O and maintain acceptable levels of agricultural production. Site-specific decisions to manage the N source, rate, time, and place for local conditions are necessary to achieve these goals. Instead of sweeping restrictions on N fertilizer useage that may not be appropriate for individual situations, well-trained crop advisors may be the most effective at guiding farmers in adopting the best available technology for specific fields.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

Conclusion

Crop recovery of applied N by annual cereal grain crops in the field is often below 40 to 50%, but can be raised to 60 to 70% or more through more intensive management (*54*). Because of relatively low crop N recovery, the heightened risks of N loss to the environment with increased N use, and the potential negative consequences of the losses, the U.S. Environmental Protection Agency Integrated Nitrogen Committee calls for a 25% improvement in N use efficiency over current levels (*55*).

Carefully selecting the right source, rate, time, and place of fertilizer N applications can result in improved crop N recovery, increased crop yields, and lessen undesirable environmental impacts. As a result of improved management, significant gains in crop N recovery are within practical reach. Optimizing N management to minimize the surplus or residual N, can reduce the risks of N loss via the various N loss pathways, and minimize N_2O emissions (*14*).

Adoption of intensive crop production techniques resulting in higher yields (including appropriate fertilizer use) has spared the emissions of significant quantities of GHGs that would have otherwise been released, if less intensive crop production techniques had been used to sustain the global food supply (*52*). This intensification must be done with the use of locally adapted management practices to protect soil, water, and air. Appropriate intensification can also optimize food production in areas where it is best suited and spare fragile natural areas (such as forests, native grasslands, and wetlands) from development (*10*). Improving fertilizer management using the 4R nutrient stewardship approach has considerable potential for mitigating the impact of GHG emissions from agricultural land.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

References

1. IPCC. *Climate change 2001: The scientific basis*; Cambridge University Press: Cambridge, UK, 2001.
2. Levin, K.; Turpak, D. *Climate Science 2008: Major New Discoveries. WRI Issue Brief, July 2009*; World Resources Institute: Washington, DC, 2009.
3. IPCC. Summary for Policymakers. In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, S., Eds.; Cambridge University Press: Cambridge, 2008.
4. Le Quéré, C.; Raupach, M. R.; Canadell, J. G.; Marland, G.; et al. Trends in the sources and sinks of carbon dioxide. *Nat. Geosci.* **2009**, *2*, 831–836.
5. Flynn, H. C.; Smith, P. *Greenhouse gas budgets of crop production – current and likely future trends*; International Fertilizer Industry Association: Paris, France, 2010.
6. Stewart, W. M.; Dibb, D. W.; Johnston, A. E.; Smyth, T. J. The contribution of commercial fertilizer nutrients to food production. *Agron. J.* **2005**, *97*, 1–6.
7. Erisman, J. W.; Sutton, M. A.; Galloway, J.; Klimont, Z.; Winiwarter, W. 100 years of ammonia synthesis: how a single patent changed the world. *Nat. Geosci.* **2008**, *1*, 636–639.
8. IPCC. *Intergovernmental Panel on Climate Change Guidelines for National Greenhouse Gas Inventories. Volume 4: Agriculture, Forestry and Other Land Use.* Chapter 11: N_2O Emissions from Managed Soils, and CO_2 Emissions from Lime and Urea Application. 2006.
9. USEPA. *Inventory of U.S. greenhouse gas emissions and sinks: 1990-2008.* Environmental Protection Agency, Office of Atmospheric Programs: Washington, DC, 2010.
10. Gockowski, J.; Sonwa, D. *Cocoa intensification scenarios and their predicted impact on CO_2 emissions, biodiversity conservation, and rural livelihoods in the Guinea Rain forest of West Africa*; Environmental Management. 2010. 10.1007/s00267-010-9602-3.
11. Burney, J. A.; Davis, S. J.; Lobell, D. B. Greenhouse gas mitigation by agricultural intensification. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 12052–12057.
12. Linn, L. M.; Doran, J. W. Effect of water-filled pore space on carbon dioxide and nitrous oxide prodouction in tilled and nontilled soils. *Soil Sci. Soc. Am. J.* **1984**, *48*, 1267–1272.
13. Snyder, C. S.; Bruulsema, T. W.; Jensen, T. L.; Fixen, P. E. Review of greenhouse gas emissions from crop production systems and fertilizer management effects. *Agric. Ecosyst. Environ.* **2009**, *133*, 247–266.
14. Van Groenigen, J. W.; Velthof, G. L.; Oenema, O.; Van Groenigen, K. J.; Van Kessel, C. Towards an agronomic assessment of N_2O emissions; a case study for arable crops. *Eur. J. Soil Sci.* **2010**, *61*, 903–913.
15. Bruulsema, T. W.; Witt, C.; García, F.; Li, S.; Rao, T. N.; Chen, F.; Ivanova, S. A global framework for fertilizer BMPs. *Better Crops* **2008**, *92* (2), 13–15.

16. Snyder, C. S. Fertilizer Nitrogen BMPs to Limit Losses that Contribute to Global Warming; International Plant Nutrition Institute: Norcross, GA, June 2008; Ref. # 08057.
17. IPNI. *The 4Rs: Right Source, Right Rate, Right Time, Right Place*. Available online at http://www.ipni.net/4R. International Plant Nutrition Institute: Norcross, GA, 2010.
18. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. Emissions of N_2O and NO from fertilized fields: summary of available measurement data. *Global Biogeochem. Cycles* **2002**, *16* (6), 1–13.
19. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. Modeling global annual N_2O and NO emissions from fertilized fields. *Global Biogeochem. Cycles* **2002**, *16*, 28–1, 28–8.
20. Stehfest, E.; Bouwman, L. N_2O and NO emission from agricultural fields and soils under natural vegetation: summarizing available measurement data and modeling of global annual emissions. *Nutr. Cycling Agroecosyst.* **2006**, *74*, 207–228.
21. Venterea, R. T. Nitrite-driven nitrous oxide production under aerobic soil conditions: kinetics and biochemical controls. *Global Change Biology* **2007**, *13*, 1798–1809.
22. Kool, D. M.; Wrage, N.; Zechmeister-Boltenstern, S.; Pfeffer, M.; Brus, D.; Oenema, O.; Van Groenigen, J.-W. Nitrifier denitrification can be a source of N_2O from soil: a revised approach to the dual-isotope labelling method. *Eur. J. Soil Sci.* **2010**, *61*, 759–772.
23. Harrison, R.; Webb, J. A review of the effect of N fertilizer type on gaseous emissions. *Adv. Agron.* **2001**, *73*, 65–108.
24. Chen, D.; Freney, J. R.; Rochester, I.; Constable, G. A.; Mosier, A. R.; Chalk, P. M. Evaluation of a polyolefin coated urea (Meister) as a fertilizer for irrigated cotton. *Nutr. Cycling. Agroecosyst.* **2008**, *81*, 245–254.
25. Breitenbeck, G. A.; Bremner, J. M. Effects of various nitrogen fertilizers on emission of nitrous oxide from soils. *Biol. Fert. Soils* **1986**, *2*, 195–199.
26. Venterea, R. T.; Burger, M.; Spokas, K. A. Nitrogen oxide and methane emissions under varying tillage and fertilizer management. *J. Environ. Qual.* **2005**, *34*, 1467–1477.
27. Venterea, R. T.; Dolin, M. S.; Oschner, T. E. Urea decreases nitrous oxide emissions compared with anhydrous ammonia in a Minnesota corn cropping system. *Soil Sci. Soc. Am. J.* **2010**, *74*, 407–418.
28. Venterea, R. T.; Stanenas, A. J. Profile analysis modeling and modeling of reduced tillage effects on soil nitrous oxide flux. *J. Environ. Qual.* **2008**, *37*, 1360–1367.
29. Burton, D. L.; Li, X.; Grant, C. A. Influence of fertilizer nitrogen source and management practice on N_2O emissions from two Black Chernozemic soils. *Can. J. Soil Sci.* **2008**, *88*, 219–227.
30. Mosier, A. R.; Duxbury, J. M.; Freney, J. R.; Heinemeyer, O.; Minami, K. Nitrous oxide emissions from agricultural fields: assessment, measurement and mitigation. *Plant Soil* **1996**, *181*, 95–108.
31. Hyatt, C. R.; Venterea, R. T.; Rosen, C. J.; McNeary, M.; Wilson, M. L.; Dolan, M. S. Polymer-coated urea maintains potato yields and reduces nitrous

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

oxide emissions in a Minnesota loamy sand. *Soil Sci. Soc. Am. J.* **2010**, *74*, 419–428.

32. Halvorson, A. D.; Del Grosso, S. J.; Alluvione, F. Nitrogen source effects on nitrous oxide emissions form irrigated no-till corn. *J. Environ. Qual.* **2010**, *39*, 1554–1562.
33. Shaviv, A. Advances in controlled release fertilizers. *Adv. Agron.* **2000**, *71*, 1–49.
34. Chien, S. H.; Prochnow, L. I.; Cantarella, H. Recent developments of fertilizer production and use to improve nutrient efficiency and minimize environmental impacts. *Adv. Agron.* **2009**, *102*, 267–322.
35. Parkin, T. B.; Hatfield, J. L. Influence of nitrapyrin on N_2O losses from soil receiving fall-applied anhydrous ammonia. *Agric. Ecosyst. Environ.* **2010**, *136*, 81–86.
36. Akiyama, H.; Yan, X.; Yagi, K. Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N_2O and NO emissions from agricultural soils: meta-analysis. *Global Change Biol.* **2010**, *16*, 1837–1846.
37. Halvorson, A. D.; Del Grosso, S. J.; Reule, C. A. Nitrogen, tillage, and crop rotation effects on nitrous oxide emissions form irrigated cropping systems. *J. Environ. Qual.* **2008**, *37*, 1337–1344.
38. Millar, N.; Robertson, G. P.; Grace, P. R.; Gehl, R. J.; Hopben, J. P. Nitrogen fertilizer management for nitrous oxide (N_2O) mitigation in intensive corn (Maize) production: an emissions reduction protocol for US Midwest agriculture. *Mitigation Adapt. Strategies Global Change* **2010**, *15*, 185–204.
39. McSwiney, C. P.; Robertson, G. P. Nonlinear response of N_2O flux to incremental fertilizer addition in a continuous maize (*Zea mays* L.) cropping system. *Global Change Biol.* **2005**, *11*, 1712–1719.
40. Adviento-Borbe, M. A. A.; Haddix, M. L.; Binder, D. L.; Walters, D. T.; Dobermann, A. Soil greenhouse gas fluxes and global warming potential in four high-yielding maize systems. *Global Change Biol.* **2007**, *13*, 1972–1988.
41. Stanford, G. Assessment of soil nitrogen availability. In *Nitrogen in Agricultural Soils*; Stevenson, F. J., Ed.; Agron. Monogr. 22, American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America: Madison, WI, 1982; Ch. 17, pp 651−688.
42. Meisinger, J. J. Evaluating plant-available nitrogen in soil-crop systems. In *Nitrogen in Crop Production*; Hauck, R. A., Ed.; American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America: Madison, Wisconsin, 1984; Chapter 26, pp 391−417.
43. Crutzen, P. J.; Mosier, A. R.; Smith, K. A.; Winiwarter, W. N_2O release from agrobiofuel production negates global warming reduction by replacing fossil fuels. *Atmos. Chem. Phys.* **2008**, *8*, 389–395.
44. Randall, G. W.; Goss, M. J. Nitrate losses to surface water through subsurface, tile drainage. In *Nitrogen in the Environment: Sources, Problems, and Management*; Follett, R. F., Hatfield, J. L., Eds.; Elsevier: Amsterdam, The Netherlands, 2001; Chapter 5, pp 95−123.
45. Raun, W. R.; Solie, J. B.; Johnson, G. V.; Stone, M. L.; Mullen, R. W.; Freeman, K. W.; Thomason, W. E.; Lukina, E. V. Improving nitrogen use

efficiency in cereal grain production with optical sensing and variable rate application. *Agron. J.* **2002**, *94*, 815–820.

46. Scharf, P. C.; Lory, J. A. Calibrating reflectance measurements to predict optimal sidedress nitrogen rate for corn. *Agron. J.* **2009**, *101*, 615–625.
47. Del Grosso, S. J.; Parton, W. J.; Mosier, A. R.; Walsh, M. K.; Ojima, D. S.; Thornton, P. E. DAYCENT National-scale simulations of nitrous oxide emissions from cropped soils in the United States. *J. Environ. Qual.* **2006**, *35*, 1451–1460.
48. Griggs, B. R.; Norman, R. J.; Wilson, C. E., Jr.; Slaton, N. A. Ammonia volatilization and nitrogen uptake for conventional and conservation tilled dry-seeded, delayed -flood rice. *Soil Sci. Soc. Am. J.* **2007**, *71*, 745–751.
49. Hultgreen, G.; Leduc, P. *The effect of nitrogen fertilizer placement, formulation, timing, and rate on greenhouse gas emissions and agronomic performance*; Final Report, Project No. 5300G, ADF#19990028; Saskatchewan Dep. Agric. and Food, Regina, SK2003;
50. Drury, C. F.; Reynolds, W. D.; Tan, C. S.; Welacky, T. W.; Calder, W.; McLaughlin, N. B. Emissions of nitrous oxide and carbon dioxide: influence of tillage type and nitrogen placement depth. *Soil Sci. Soc. Am. J.* **2006**, *70*, 570–581.
51. Breitenbeck, G. A.; Bremner, J. M. Effects of rate and depth of fertilizer application on emission of nitrous oxide from soil fertilized with anhydrous ammonia. *Biol. Fertil. Soils* **1986**, *2*, 201–204.
52. Liu, X. J.; Mosier, A. R.; Halvorson, A. D.; Zhang, F. S. The impact of nitrogen placement and tillage on NO, N_2O, CH_4 and CO_2 fluxes from a clay loam soil. *Plant Soil* **2006**, *280*, 177–188.
53. Noellsch, A. J.; Motavalli, P. P.; Nelson, K. A.; Kitchen, N. R. Corn response to conventional and slow-release nitrogen fertilizers across a claypan landscape. *Agron. J.* **2009**, *101*, 607–614.
54. Kitchen, N. R.; Goulding, K. W. T. On-farm technologies and practices to improve nitrogen use efficiency. In *Nitrogen in the Environment: Sources, Problems, and Management*; Follett, R. F., Hatfield, J. L., Eds.; Elsevier: Amsterdam, The Netherlands, 2001; Chapter 13, pp 335−370.
55. USEPA. *Hypoxia in the Northern gulf of Mexico*; Environ. Protectionon Agency Science Advisory Board: Washington, DC, 2007. EPA-SAB-08-003.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch008

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Chapter 9

Physical and Chemical Manipulation of Urea Fertilizer To Limit the Emission of Reactive Nitrogen Species

M. I. Khalil*,[1,2]

[1]School of Biology and Environmental Science, University College Dublin, Belfield, Dublin 4, Republic of Ireland
[2]Climate Change Research Programme, Environmental Protection Agency, Johnstown Castle Estate, Wexford, Republic of Ireland
*E-mail: i.khalil@epa.ie; khalil_ibrahim@yahoo.com

Due to well established global warming concerns, technological attempts have been made to decrease reactive nitrogen (N) species emitted from the application of urea fertilizer to agricultural soils. This chapter summarizes previous work which investigates the mitigation potential for ammonia (NH_3), nitrogen oxides (NO_x) and nitrous oxide (N_2O), which is a potent greenhouse gas, from arable lands. Specifically, the studies examined urea granule size, depth of placement, and contribution of chemical inhibitors. Relatively large urea granule (referred to as Urea Super Granule, USG; ~10 mm) inhibited nitrification up to 7 weeks and reduced both NH_3 and NO_x emissions up to 94%, compared to normal urea size. Under cropped conditions, the USG point-placed at 7.5 cm depth showed similar N_2O emissions as urea prills (0.20-0.21% of the N applied) but increased to 0.51% under relatively higher soil moisture conditions. Surface application of urease inhibitor (phosphoric acid diamide-amended urea) decreased NH_3 volatilization up to 50%. Compared to surface application, a modified version of the inhibitor (substituted phosphoric acid triamide) mixed with the soil reduced N_2O emissions by 47%. Nitrification inhibitor (Dicyanamide plus triazole) inhibited nitrification up to 5 weeks and reduced N_2O emissions up to 60%. A combination of the urease and nitrification inhibitors

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

has the potential to limit NH_3 emissions and decrease N_2O losses up to 52%. Both deeper placement of USG and the combination of urease and nitrification inhibitors can mitigate the urea-induced emissions of reactive gaseous N species substantially.

Keywords: Urea fertilizer; nitrification; trace gases; mitigations; arable crop

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Introduction: Perspectives and Progress of Urea Forms in Reducing Reactive N Species

Reactive gaseous N species [NH_3, nitrogen oxides ($NO_x = NO + NO_2$) and N_2O] have great potential to cause environmental damage through processes such as global warming, stratospheric ozone layer depletion and acid deposition. Ammonia volatilization occurs through hydrolysis by reacting with enzyme urease, and NO_x and N_2O form in soils mainly through nitrification and denitrification, both direct and indirect. These chemical and biological reactions release gaseous N species into atmosphere under favorable soil and environmental conditions (*1–4*). Technological options are being researched globally to reduce gaseous N emissions from agricultural soils. Of particular concern are emissions associated with urea fertilizer, which is the cheapest and most widely used synthetic N fertilizer (>50% of global total nitrogenous fertilizers). Urea is an alkaline-hydrolyzing N fertilizer and is commonly available in the forms of small granules (<1 mm). It is also the main source of a number of key components of atmospheric N.

The use of urea super granule (USG>10 mm) is gaining popularity in rice-growing areas, both irrigated or rainfed, due to greater agroeconomic benefits and less N losses (*5*). However, the potential of USG in reducing gaseous N losses in dry land crop production has got little attention. Under aerobic conditions, highly localized urea/NH_4^+, NO_2^- levels and specific soil pHs develop through enzyme-catalyzed urea hydrolysis in the placement zone of USG and diffuse slowly outward. This results in either little or no immobilization initially and inhibition of both urease and nitrification activity (*6*) compared to reduced gaseous N emissions (*3*, *7*).

Both surface-applied urea prills (PU) and shallow-placed USG in coarse-textured soils increase NH_3 volatilization (*1*, *8*, *9*). High soil NH_4^+ concentrations can also result in high NO_x emissions under aerobic conditions (*10*). Mixing urea with soils, banded/deep placement, immediate rainfall/irrigation and rapid drying of the surface soil after application might reduce N losses (*11*, *12*). Reduction of N losses in deep or point-placed urea (*13*), USG in a clay soil (*14*), an alfisol (*15*), and medium to fine textured soils under upland rice and barley (*16*, *17*) has been observed. In previous laboratory studies (*3*, *11*), it was reported that deeper placement of USG can reduce NH_3 and NO_x emissions substantially compared to broadcasting/mixing PU with soils. The USG-induced

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

N_2O emissions were found to be lower from coarse to medium textured soils (0.53-0.59%) than from a clay soil (2.61%; 3), though emissions (1.24%) from a silt loam was also reported (*18*).

Studies on various urease and nitrification inhibitors as well as the combination of both with different chemistry have shown substantial reduction of gaseous N emissions from agricultural soils. The urease inhibitors, N-(n-butyl) thiophosphoric triamide (NBPT, commercially available as Agrotain®) and hydroquinone (HQ) reduced NH_3 loss efficiently (*19*, *20*). The nitrification inhibitor dicyandiamide (DCD) amended urea reduced N_2O emissions but its efficacy in limiting NH_4^+ oxidation was short-term compared to 3,4-dimethypyrazole phosphate (DMPP; (*21*, *22*)). The NBPT, DCD, and NBPT + DCD-amended urea applied to a maize field were found to reduce N_2O emission by 37.7%, 39.0%, and 46.8%, respectively, over urea alone (*23*). The effects of urease inhibitor (phospohoric acid diamide; PAD; P204/98; 0.2%) on NH_3 volatilization and of nitrification inhibitor (DCD plus 1H-1,2,4-triazole, DCD/TZ; commercially available as Alzon ® 46), both developed by the SKWP GmbH in Germany, on N_2O emissions were tested and found to have capacity to decrease N losses substantially (*24–26*).

A single compound, like DCD, demonstrated lower efficacy, higher volatility, greater instability, and a higher decomposition rate. Consequently, the need to apply larger doses of that compound may enhance NH_3 volatilization loss. The combination of two nitrification inhibitors (e.g., DCD/TZ) resulted in a synergistic effect, which enhanced nitrification inhibition efficiency by prolonging the conversion duration of the fertilizer and allowed the dosage to be reduced (*27*). In recent times, SKWP introduced a new urease inhibitor at a lower concentration (substituted phosphoric acid triamide, sPAT; P101/04; 0.06%) than (PAD, P204/98; 0.2%), and a combination of urease and nitrification inhibitor (PAD + DCD/TZ refers to UNI). Urea produced with mixing either inhibitor is available in granular form, which is larger (2-3 mm) than the PU form. This chapter evaluates the comparative efficacy of the above-mentioned physical and chemical manipulation of urea fertilizer in limiting nitrification and decreasing the emission of reactive N species (NH_3, NO_x and N_2O) from upland crop fields (*3*, *24–26*, *28*, *29*).

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Inhibiting Nitrification: Influence of Urea Granule Size and Inhibitors

Nitrification is one of the key processes in the soil-plant system with particular reference to soil fertility and productivity but makes available the substrate for subsequent formation of gaseous N species. This process is universal and rapid in aerobic soil systems, occurring mainly through biological oxidation of NH_4^+ to NO_2^- and NO_3^-. The extent however depends on the availability of substrate as NH_4^+ (either added or mineralized), soil-environmental conditions and the associated microorganisms. Any attempts to depress the activities of nitrifiers result in limited/retarded oxidation of NH_4^+ and thereby decrease leaching losses of NO_3^- and the formation of reactive gaseous N compounds (NO_2, NO and N_2O) during both nitrification and denitrification from anaerobic microsites. Other than management options, there are few reported works on limiting nitrification particularly using large urea granules applied to upland crops. There are numerous chemical compounds that can limit nitrification but only a few have been examined to find their affectivity under field conditions, for example, Nitrapyrin, DCD and a recently released DMPP (*21*, *22*). However, a single chemical compound may be incompatible in limiting nitrification (*27*) and thereby reducing gaseous N losses across soil and land use types.

To assess the potential of nitrification inhibitor (DCD/TZ) compared to urea granule size in delaying nitrification, Khalil et al. (*29*) carried out a greenhouse experiment in a loess (silt loam) soil cropped to spring wheat experiencing all natural weather conditions except rainfall, which was substituted by watering. The treatments consisted of three urea sizes: prills (PU <1 mm), granule (GU 2-3 mm) and urea super granule (USG ~10 mm) and two inhibitors: urease inhibitor (sPAT: P101/04, 0.06%), and the UNI, applied at 88.2 kg N ha^{-1}. The size of the inhibitors-amended urea was similar to the GU. The USG was point-placed at 5 cm depth, and for the other treatments, urea was mixed the soil down to a 5 cm depth.

Differential responses of the urea granule sizes and inhibitors to nitrification inhibition were anticipated through changes in mineral N (NH_4^+ and NO_3^-) overtime. During the 70-day growth period of spring wheat, they observed (*29*) significant variations of the soil NH_4^+ concentrations for all treatments until 35 days after fertilization only (Fig. 1a). The PU and GU showed a faster disappearance of NH_4^+ from the soil, attributing to mainly rapid nitrification associated with the application of smaller urea granules, than the USG and urea amended with inhibitors (sPAT and UNI). This is in conformity with the increased accumulation of NO_3^- observed over time (Fig. 1b). The maximum NO_3^- level at 35 days after fertilization with the USG indicates a delayed nitrification for 7 weeks. Likewise, Tenuta and Beauchamp (*18*) from three laboratory experiments with urea granules or a high concentration of urea prills found lower rates of NH_4^+ disappearance, signifying the nitrification process was adversely affected. In a similar laboratory study using various urea granule sizes, Khalil et al. (*3*) also observed a delay in nitrification for several weeks.

The responses of UNI and sPAT in limiting nitrification were slower, attributing somewhat to hydrodynamic dispersion or dissolution of inhibitor-amended small granules than the point-placed USG. The efficacy of sPAT in limiting nitrification is probably due to the delayed hydrolysis and the resultant nitrification impediment. As evident from a laboratory study (*29*), the delay in nitrification with the nitrification inhibitor DCD/TZ was smaller, and even with the UNI (5 weeks). The affectivity of DCD or 3,4-dimethypyrazole phosphate (DMPP) (*21*, *22*, *30*) and/or in combination of DCD and NBPT (*23*, *31*) has been reported to last for up to 8 weeks after N application. The impact differences between the nitrification inhibitors in the control of nitrification are probably linked to the higher mobility of inhibitors, the type of N fertilizer, and the variable temperatures. Over time total mineral N varied marginally between the urea granule size and inhibitors, and NO_3^- took the major share at later periods (*29*). However, the USG overall retained more mineral N compared with the sPAT and

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

UNI treatments. The findings signify that both the USG and urea amended with inhibitors (DCD/TZ and UNI) could effectively limit nitrification from 5-7 weeks, which is in accordance with laboratory (*28*, *29*) and field experiments (*24*).

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

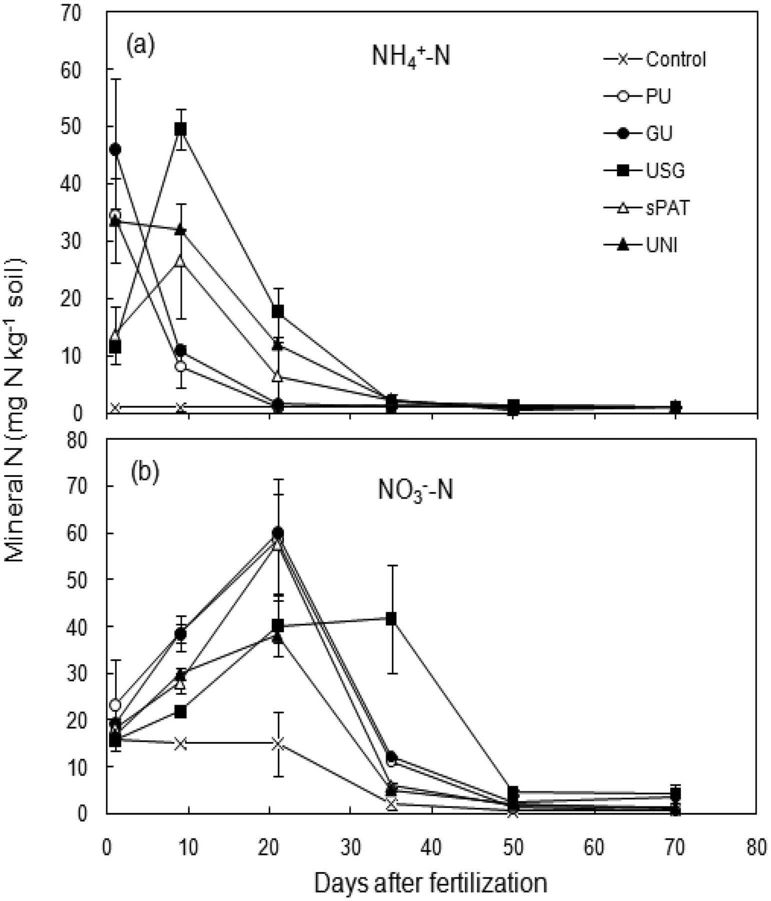


Figure 1. Soil NH_4^+- (a) and NO_3^--N (b) concentrations (mg N kg^{-1} soil) over time under greenhouse conditions cropped to spring wheat, where urea prills (PU) and granule (GU) were mixed with the soil and super granule (USG) was point-placed at 5.0 cm depth; urea granule was added with urease inhibitor (substituted phosphoric acid triamide, sPAT, 0.06%), and a combination of both urease (phosphoric acid diamide, PAD, 0.2%) and nitrification (dicyandiamide plus 1H-1,2,4-triazole, DCD/TZ) inhibitors (UNI). Vertical bars and arrows indicate standard errors. (Reproduced from reference (29)).

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Minimizing NH_3 Loss: Impact of Urea Granule Size and Urease Inhibitor

Urea is subject to NH_3 volatilization particularly when surface-applied (broadcast), and later top- or side-dressed, during the growth period of upland crops. The associated NH_3 loss increases with increasing hydrolysis rate, soil pH and N fertilizer rate. This loss is one of the major concerns towards poor N use efficiency and natural ecosystem degradation. Thus, strategic abatements of NH_3 volatilization from agroecosystems are imperative. It has been demonstrated that either PU mixed with the soil or amended with urease inhibitors (NBPT, HQ, etc.) reduces NH_3 loss substantially (*19*, *20*). The level of loss is severely higher in tropics due to rapid hydrolysis at favorable climatic, soil and management as compared to temperate zones. However, poorly understood is the chemical nature in which the urease inhibitor degrades in an agroecoystem and thereby its effectiveness to minimize NH_3 loss. Recently, urea soil mixing, large urea granules and use of other chemical origins (phosphoric acid diamide/triamide) either alone or in combination with nitrification inhibitor has been tested to decrease NH_3 volatilization losses.

In a greenhouse study, Khalil et al. (*28*) investigated the influence of USG placement depths (point-placed at 2.5, 5 cm and 7.5 cm; applied at 91.74 kg N ha^{-1}) on NH_3 volatilization measured for 43 days using a dynamic chamber method, including simultaneous measurement of NO_x emission. Irrespective of USG placement depths the reported maximum peaks for NH_3 was 8 days after fertilization; there was a delay of hydrolysis for some days with reductions to about zero emissions by day 15 (Fig. 2a). The USG point-placed near to soil surface (2.5 cm) demonstrated a several-fold higher NH_3 flux than the deeper placements (Fig. 2b), ranging from 0.07 to 1.22% of the urea-N applied. The enhanced NH_3 loss from shallower placement was likely due to vapor diffusion from USG-induced high NH_4^+ concentration. The deeper placement of USG decreased NH_3 emission by 79-94% over the shallower placement. This may be attributed to the effects of high H^+ buffering capacities to fix NH_3 vapor within the upper soil layer and the inhibition of urease activity by high urea concentration (enzyme denaturizing). In another laboratory study, Khalil et al. (*3*) found highest N losses from the PU-treated treatment (1.73%) and regardless of soil type, the larger urea granules did not emit more than 0.27% of the added N over 22 days. This signifies that NH_3 volatilization decreases with increasing granule size and the mixing of PU deeper into the soil reduces NH_3 volatilization greatly as compared to USG point-placed and/or banding of urea (*3*, *4*, *6*, *11*).

To examine the influence of urease inhibitor phosphoric acid diamide (PAD) on NH_3 and NO_x emission, a series of experiments were carried out by other researchers (*24–26*). They conducted the experiments for three consecutive years with surface application of urea at 80 kg N ha^{-1} four times during spring and summer to winter wheat. Schraml et al. (*26*) did not find any significant difference in reducing NH_3 loss between the PAD and NBPT. The reported loss was 2.6 kg NH_3-N ha^{-1} and the efficiency of the inhibitors was consistent on average in decreasing the loss by 50% (Fig. 2c). However, the inhibition of urease activity was observed to be prolonged mainly during early spring season. The large variation in NH_3 loss was associated with the substantial emission divergences due to application timing differences within and between the years.

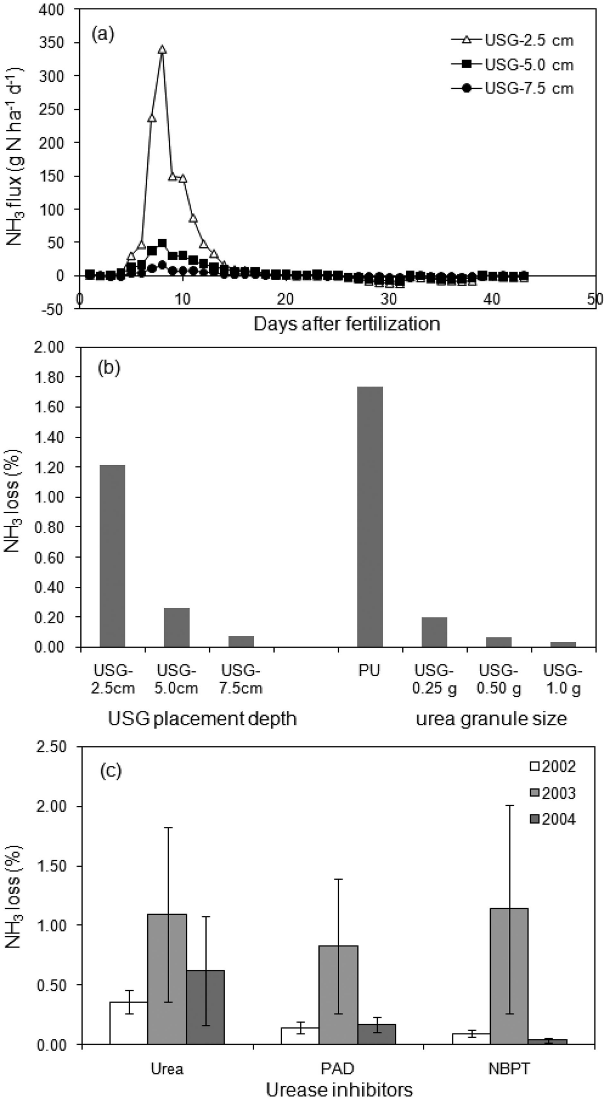


Figure 2. NH_3 volatilization rates, g N ha^{-1} d^{-1} (a) and losses, % (b) as influenced by urea super granule (USG) placement depths (2.5, 5.0 and 7.5 cm) and urea granule sizes (PU = urea prills, USG weights of 0.25, 0.50 and 1.0 g) (Reproduced from references (3, 28)). NH_3 losses (%) from the application of urea and urea amended with urease inhibitors (PAD = phosphoric acid diamide and NBPT = N-(n-butyl) thiophosphoric triamide) (c; Reproduced from references (24, 26)). Vertical bars and arrows indicate standard errors.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Results clearly denote that both deeper (<5 cm) placement of USG, an approach which is associated with soil covering, and the use of urease inhibitors is more practical and efficient in reducing NH_3 volatilization. Similar effectiveness may also be found even when PU is mixed with the soil. Nevertheless, the decrease in NH_3 volatilization and delay in nitrification with USG technology in particular could equally have large potential of supplying N in NH_4^+ form for later uptake by plants as compared to urease inhibitors. This may be highly relevant in a situation where an intensive and large irrigation event may not cause severe hydrodynamic dispersion of mineral N.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Decreasing NO_x Emissions: Effect of Urea Granule Size and Urease Inhibitors

Nitrogen oxides (NO_x = NO + NO_2; mainly in the form of NO) are also produced as intermediates during microbial nitrification and denitrification in soils. The amount of its production depends mainly on the rate of N fertilizer application, associated microbial activity and environmental factors.

Khalil et al. (*28*) examined the impact of USG point-placed at 2.5, 5 cm and 7.5 cm applied at 91.74 kg N ha^{-1} in a loess soil cropped to spring wheat on NO_x emission. The maximum NO_x emission peaked at 31 days after fertilization and thereby started to increase when NH_3 volatilization was declining (Fig. 3a). Analogous to NH_3 loss, the deeper USG placements reduced total NO_x emission by 23 and 88% over the shallower placement. This means that the production and release of both gases (NH_3 and NO_x) are triggered by similar soil and environmental conditions, relating mainly to aerobic situations. This is in accordance with the results of another study (*3*) which had noticeably higher NO_x emission from the PU-treated soil (0.97%) than from the larger granule sizes (0.09-0.29%), ascribing to positional differences in the concentration of mineral N and nitrification. Similar findings were also reported from an experiment where urea was band-placed at 12 cm depth (*32*). The presence of solution and gas phase of soils or soil consumption limits NO_x emissions (*3*, *32*, *33*) and its formation processes are extremely temporally and spatially heterogeneous (*34*). The NO_x emission enhances in the presence of comparatively large NH_4^+ for subsequent nitrification in surface layers (*3*, *35*) and so long as intraspecific soil moisture differences do not limit the process.

Schraml et al. (*26*) also compared the effectiveness of the PAD with the NBPT following surface application of urea at 80 kg N ha^{-1} four times during spring and summer to winter wheat. Regardless of urea and urea amended with the urease inhibitors, the NO_x emission was low (Fig. 3b). On average, both inhibitors reduced the emission by 10%. In contrast to the application of USG, the drop of NH_3 losses by means of urease inhibitors was found to have no influence on NO_x emissions. Compared to the use of urease inhibitors-amended urea, the USG technology could have larger potential to reduce NO_x emission from upland systems. However, further study on the potential of physically manipulated urea over the amendment of chemicals in reducing both NH_3 and NO_x emission would be needed to draw conclusions.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

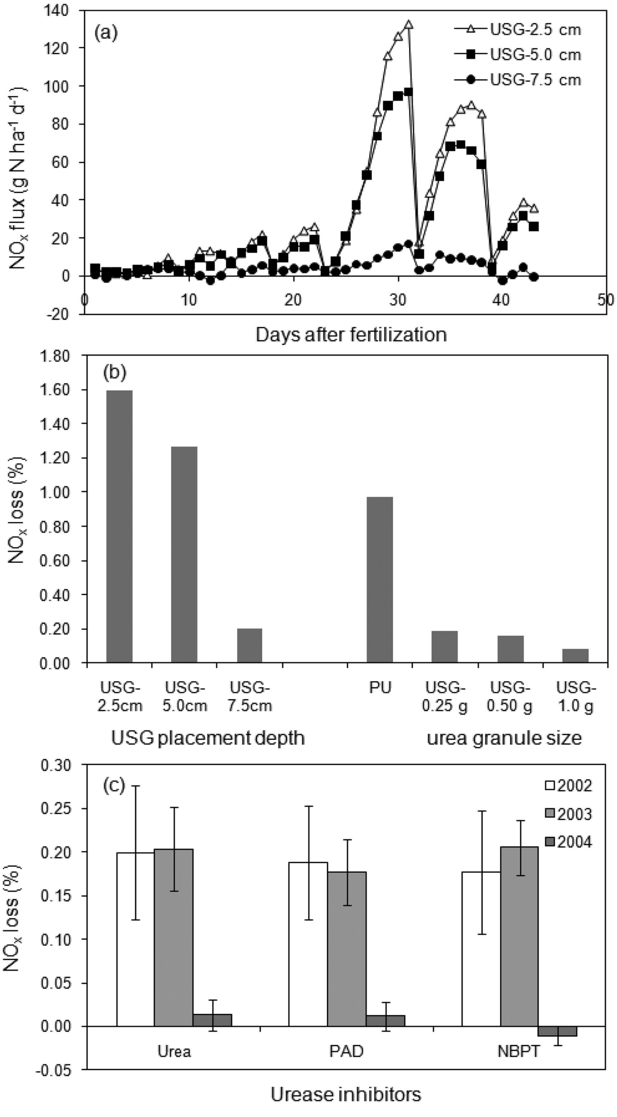


Figure 3. NO_x emission rates, g N ha^{-1} d^{-1} (a) and losses, % (b) as influenced by urea super granule (USG) placement depths (2.5, 5.0 and 7.5 cm) and granule sizes (PU =urea prills, USG weights of 0.25, 0.50 and 1.0 g) (Reproduced from references (3, 28)). NO_x losses (%) from the application of urea and urea amended with urease inhibitors (PAD = phosphoric acid diamide and NBPT = N-(n-butyl) thiophosphoric triamide) (c; Reproduced from references (24, 26)). Vertical bars and arrows indicate standard errors.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Reducing N_2O Emissions: Contribution of Urea Granule Size and Inhibitors

Atmospheric build-up of N_2O, which is a powerful GHG gas, has significant global environmental consequences. Despite large uncertainties, the contribution of agricultural practices to global N_2O budget accounts for 80% of anthropogenic emissions. N_2O is formed mainly through two biological processes in agricultural soils, as an intermediate during nitrification (aerobic process) and/or during denitrification (anaerobic process) either directly or from anaerobic microsites. The degree of N_2O emissions from these processes depends on the availability of substrates, associated microorganisms as well as favorable soil and environmental conditions (*36*). In upland soils, crop management includes type, timing and amount of N fertilizer application, which has several constraints as a single strategy to limit nitrification and resultant N_2O emissions (*37*). Improvement of agronomic N use efficiency by suppressing nitrification to keep N in NH_4^+ form for a longer time for plant uptake is a key. For this, use of slow-release fertilizers and particularly nitrification inhibitors of various chemical origins would have further advantages to mitigate N_2O emissions but are still not widely or efficiently implemented.

Khalil et al. (*28*) carried out a greenhouse experiment for 116 days in a loess soil cropped to spring wheat to distinguish the impact of USG point-placed at 7.5 cm with PU mixed homogenously with the soil applied at 88.15 kg N ha^{-1} on N_2O emissions measured using a static chamber method. Following application of urea fertilizer, the maximum peak for N_2O flux appeared earlier in the PU treatment presumably due to rapid nitrification, which was greater than in the USG (Fig 4a). The USG exhibited slightly higher N_2O fluxes at later periods of measurement, attributing to the delayed nitrification and thereby more N storage, compared to the PU. However, total N_2O emissions from both urea sizes varied significantly only with unfertilized control (Table 1). As observed for nitrification, the USG also delayed N_2O emissions for 2-3 weeks. In effect, however, no difference in the relative (0.20-0.21%) or actual (0.01% of the added ^{15}N) losses of added urea-N as N_2O between the two granule sizes were noticed (Table 1). A similar delay in both nitrification and N_2O emissions was also evident in another laboratory study with urea granule size and placements under non-cropped conditions (*6*).

Khalil et al. (*28*) also investigated, in a greenhouse under controlled environmental conditions, the influence of USG placement depths (point-placed 2.5, 5.0 and 7.5 cm) applied at 91.74 kg N ha^{-1} on N_2O emissions measured during a 70-day growth period of spring wheat. By 27 days after fertilization, the USG point-placed at 5 cm demonstrated the maximum peak for N_2O flux, which was followed by the USG point-placed at 2.5 and 7.5 cm (Fig. 4b). The USG placement depths were found to have no significant influences on total emissions but the relative losses of added N as N_2O ranged between 0.50 and 0.73%. The higher losses ascribe to higher soil moisture-associated contribution of simultaneous nitrification and denitrification to N_2O emissions (*36*), compared to the previous study. The ^{15}N tracer study showed that the contribution of added N to N_2O emissions increased with increasing USG placement depths (*3*, *6*, *18*) but decreased over time and was small (0.02-0.15%; Table 1). The above

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

N_2O emissions are consistent with other experiments conducted at moisture levels below and above field capacities using various urea granule sizes in light to medium-textured soils (0.17 to 0.50% of the added N) (*29*), except for clay (2.61%) (*3*). Overall, the difference can be narrowed if areas receiving equal N of either granule size are considered. This is in line with another work (*29*) where the maximum peaks for N_2O was observed by 13 days after fertilization, showing the highest with the GU (Fig. 4c) and the relative N_2O losses did not vary significantly between urea granule sizes (Table 2). These findings signify the large potential of USG in reducing N_2O emission where the emission factors are much lower than the Intergovernmental Panel on Climate Change (IPCC) Guidelines (1%, (*38*)).

Khalil et al. (*29*) further examined the potentials of the urease (sPAT) and combination of urease and nitrification inhibitors (UNI) in reducing N_2O emissions. They did not include nitrification inhibitor (DCD/TZ) due primarily to the negligible impact difference between DCD/TZ and UNI in relative loss of N_2O, ranging between 0.08 and 0.14% of urea-N applied. The efficacy of DCD/TZ as a nitrification inhibitor was evaluated in a preliminary study by Weber et al. (*25*), showing a 60% reduction of urea fertilizer-induced N_2O emissions. Though lower than above and highly variable, it has been reported that the nitrification inhibitor alone either as DCD, which may stimulate NH_3 volatilization, or DMPP decreased N_2O emissions between 20 and 53% in wheat and barley systems (*19*, *21*, *22*, *39*–*41*).

Table 1. Total N_2O flux, its relative and fertilizer N losses over 116 (experiment I) and 70 days (experiment II) growth periods of spring wheat as influenced by urea granule size, methods and depths of placement. (Reproduced from reference (*28*))

Parameters	*Experiment I*				*Experiment II*				
	Cont.	*PU*	*USG-7.5*	*$LSD_{0.05}$*	*Cont.*	*USG-2.5*	*USG-5.0*	*USG-7.5*	*$LSD_{0.05}$*
Total N_2O emission (g N ha^{-1})	180.3	364.8	370.3	125.8	142.9	737.0	787.3	607.4	242
Relative loss of added N as N_2O (%)		0.20	0.21	ns		0.65	0.70	0.51	ns
Fertilizer N lost as N_2O (%)		0.01	0.01	ns		0.02	0.15	0.11	0.03

Standard calculation procedures for relative and fertilizer N losses were followed. Cont. = unfertilized control; PU = prilled urea, mixed up to 7.5 cm soil depths; USG-2.5, 5.0 and 7.5 = urea super granule point-placed at 2.5, 5.0 and 7.5 cm soil depths; LSD = least significant difference at 5% level of probability.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Table 2. Total N_2O fluxes and the relative N_2O loss of added N from the experimental soil at varying urea size, urease inhibitor and the combination of urease and nitrification inhibitor under greenhouse conditions cropped to spring wheat (Experiment III). (Reproduced with permission from reference (*29*). Copyright Wiley-VCH Verlag GmbH & Co. KGaA)

Treatments		*Cont.*	*PU (<1 mm)*	*GU (2-3 mm)*	*USG (~10 mm)*	*sPAT (as GU)*	*UNI (as GU)*	*$LSD_{0.05}$*
Total N_2O flux (g N/ha)	45 day	130.3	254.6	338.7	314.2	202.8	146.0	135.7
	70 day	186.3	325.0	386.7	424.5	294.6	284.1	ns
Relative loss of added N (%)	45 day		0.14	0.24	0.21	0.08	0.02	0.20
	70 day		0.16	0.23	0.27	0.12	0.11	ns

Control = unfertilized control, PU = urea prills, GU = urea granule, USG = urea super granule, sPAT = substituted phosphoric acid triamide (urease inhibitor), DCD/TZ = dicyandiamide plus 1H-1,2,4-triazole (nitrification inhibitor), UNI = combined urease (PAD = phosphoric acid diamide) plus nitrification (DCD/TZ) inhibitors, $LSD_{0.05}$ = least significance difference at 5% level of probability.

Both UNI and sPAT delayed N_2O release and reduced the emissions by 23-31% compared to PU and by 47-52% compared to GU; GU size is similar to the size of the inhibitors (Table 2). The reason for less N_2O emissions by the soil-mixed sPAT was due to delayed hydrolysis and thereby associated N immobilization. Such findings are consistent with other studies that used hydroquinone as a urease inhibitor (*19*). However, the broadcast sPAT increased N_2O emission by 47%, attributing to less NH_3 volatilization and thereby increased retention of mineral N in the soil (*29*). In contrast to the application of sPAT and DCD/TZ separately, the UNI could bring larger benefits by reducing the respective gaseous N losses; though distinct processes are responsible but closely coupled under aerobic conditions (*23*). Overall N_2O emissions under cropped conditions were small due to the controlled soil water conditions, the relatively low N rates and the probable contribution of nitrification more than denitrification under upland systems. The UNI under both experimental conditions and the DCD/TZ under laboratory conditions acted similarly in reducing N_2O emissions, in line with other findings though differing with chemical compositions (*19*, *33*, *39*). The application of USG increased N_2O emissions to some extent but still substantially less than the IPCC default emission factor. Therefore, the USG technique should be taken into account as part of strategic N fertilizer management to decrease reactive gaseous N species from upland systems.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

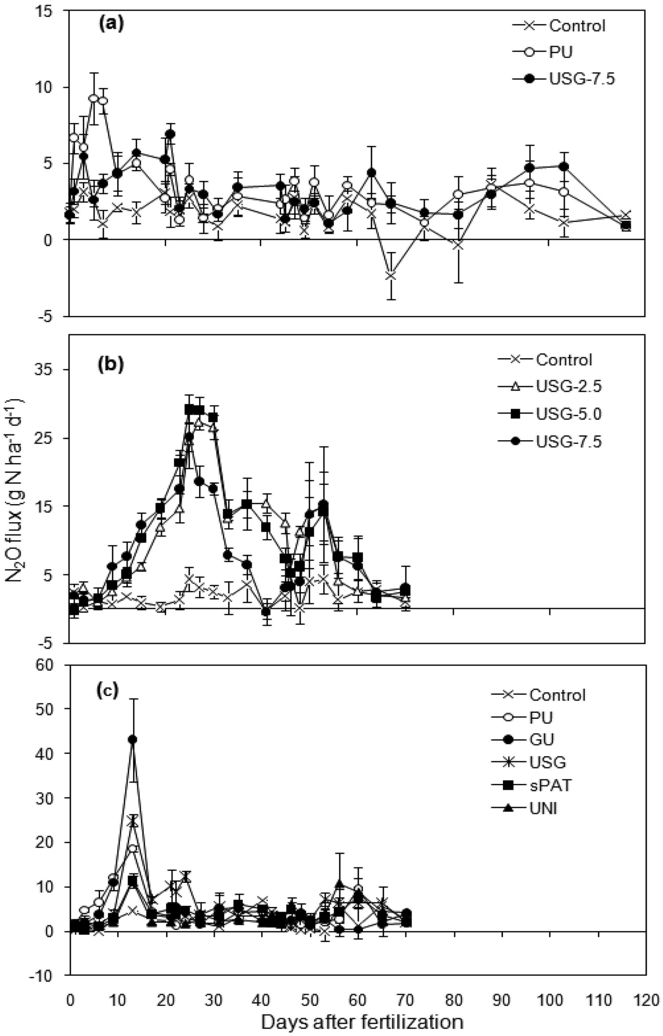


Figure 4. N_2O emission rates from two contrasting urea granule size (PU = urea prills, USG = urea super granule) during 116 days wheat growth period (a), from USG placement depths (2.5, 5.0 and 7.5 cm) during 70 days wheat growth (b) and from urease inhibitor (substituted phosphoric acid triamide, sPAT, 0.06%), and a combination of both urease (phosphoric acid diamide, PAD, 0.2%) and nitrification (dicyandiamide plus 1H-1,2,4-triazole, DCD/TZ) inhibitors (UNI) as compared with urea granule size (PU, GU = Urea granule and USG point-placed at 5 cm) during 70 days wheat growth period (c). Vertical bars and arrows indicate standard errors. (Reproduced from reference (28) and with permission from reference (29). Copyright Wiley-VCH Verlag GmbH & Co. KGaA).

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Summary

This chapter builds upon previous works dealing with mitigation of gaseous N species through physical and chemical manipulation of urea fertilizers applied to upland crops. Application of the relatively larger urea granule (USG) could be more practical and efficient in reducing NH_3 and NO_x losses as well as delaying nitrification as compared with the soil- mixing PU and the use of urease inhibitor. The USG may somewhat increase N_2O emissions relative to normal granule size but the emission potential is substantially less than the IPCC default emission factor. Importantly the USG can maintain N supply for later plant growth stages by delaying nitrification and gaseous N losses, similar to urease and nitrification inhibitors, compared to PU. The observed benefits of USG placement at deeper depths need to be tested at the field scale, and investigation of easy methods of compact USG preparation and of its application under upland conditions may be required. Soil mixing of urease inhibitor (sPAT) could decrease N_2O emission compared to surface application. The USG with added inhibitors have no advantage in terms of delaying nitrification and N_2O emissions over the combined urease plus nitrification inhibitors (UNI). Though the nitrification inhibitor (DCD/TZ) has a similar impact to reduce N_2O emissions, the coupled inhibitors UNI could also have additional potential of reducing urea-induced NH_3 and NO_x emission following either mixing or broadcasting methods. Further investigations under field conditions, including application method and timing, are necessary to determine whether the UNI is an environmentally-benign technology and to quantify any agroeconomic benefits.

Acknowledgments

The research was supported by funding from the Alexander von Humboldt Foundation and Technical University of Munich especially Prof. Urs Schmidhalter. Materials and supplied from SKW GmbH, Germany, are gratefully acknowledged. Thanks to Dr. Amrith Gunasekara, California Department of Food and Agriculture, USA and Mr. Phillip O'Brien, EPA, Ireland, for their valuable inputs in improving the manuscript.

References

1. Sommer, S. G.; Scjoerring, J. K.; Denmead, O. T. *Adv. Agron.* **2004**, *82*, 557–622.
2. Khalil, M. I.; Rosenani, A. B.; Van Cleemput, O.; Shamshuddin, J.; Fauziah, C. I. *Biol. Fertil. Soils* **2002**, *36*, 59–65.
3. Khalil, M. I.; Schmidhalter, U.; Gutser, R. *Water, Air, Soil Pollut.* **2006**, *175*, 127–148.
4. Mulvaney, R. L.; Khan, S. A.; Mulvaney, C. S. *Biol. Fertil. Soils* **1997**, *24*, 211–220.
5. Savant, S. K.; Stangel, P. J. *Ferti. Res.* **1990**, *25*, 1–83.
6. Khalil, M. I.; Schmidhalter, U.; Gutser, R. *Commun. Soil Sci. Plant Anal.* **2009**, *40*, 1191–1213.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

7. Shah, S. B.; Wolfe, M. L. *Commun. Soil Sci. Plant Anal.* **2003**, *34*, 1245–1260.
8. Buresh, R. J. *Fertil. Res.* **1987**, *12*, 263–268.
9. Zhang, S. L.; Cai, G. X.; Wang, X. Z.; Xu, Y. H.; Zhu, Z. L.; Freney, J. R. *Pedosphere* **1992**, *2*, 171–178.
10. Russow, R.; Sich, I.; Neue, H.-U. *Chemosphere: Global Change Sci.* **2000**, *2*, 359–366.
11. Bouwmeester, R. J. B.; Vlek, P. L. G.; Stumpe, J. M. *Soil Sci. Soc. Am. J.* **1985**, *49*, 376–381.
12. Khalil, M. I.; Schmidhalter, U.; Gutser, R. *Plant Nutrition for Food Security, Human Health and Environmental Protection*; Li, C. J. et al., Eds.; Tsinghua University Press: China, 2005; pp 1122−1123.
13. Roelcke, M.; Li, S. X.; Yian, X. H.; Gao, Y. J.; Richter, J. *Nutr. Cycling Agroecosyst.* **2002**, *62*, 73–88.
14. Buresh, R. J.; Vlek, P. L. G.; Stumpe, J. M. *Plant Soil* **1984**, *80*, 3–119.
15. Moraghan, J. T.; Rego, T. J.; Buresh, R. J. *Plant Soil* **1984**, *82*, 193–203.
16. Patel, S. K.; Panda, D.; Mohanty, S. K. *Fertil. Res.* **1989**, *19*, 113–119.
17. Malhi, S. S.; Nyborg, M. *Nutrient Management for Sustained Productivity*; Bajwa, M. S. et al., Eds.; Department of Soils, Punjab Agricultural University: India, 1992; pp 355−365.
18. Tenuta, M.; Beauchamp, E. G. *J. Environ. Qual.* **2000**, *29*, 1408–1413.
19. Boeckx, P.; Xu, X.; Van Cleemput, O. *Nutr. Cycl. Agroecosyst.* **2005**, *72*, 41–49.
20. Gioacchini, P. A.; Nastri, C.; Marzadori, C.; Giovannini, L. V. Antisari; Gessa, C. *Biol. Fertil. Soils* **2002**, *36*, 129–135.
21. Linzmeier, W.; Gutser, R.; Schmidhalter, U. *Biol. Fertil. Soils* **2001**, *34*, 103–108.
22. Majumdar, D.; Pathak, H.; Kumar, S.; Jain, M. C. *Agric. Ecosys. Environ.* **2002**, *91*, 283–293.
23. Ding, W. X.; Yu, H. Y.; Cai, Z. *Biol. Fertil Soils* **2011**, *47*, 91–99.
24. Weber, A.; Gutser, R.; Michel, H.-J.; Wozniak, H.; Chen, G. X.; Xu, H.; Niclas, H.-J. *Greenhouse Gas Emissions from Agriculture – Mitigation Options and Strategies*; Weiske, A., Ed.; Leipzig, Germany, 2004; pp 273−275.
25. Weber, A.; Gutser, R.; Schmidhalter, U. *Greenhouse Gas Emissions from Agriculture – Mitigation Options and Strategies*; Weiske, A., Ed.; Leipzig, Germany, 2004; pp 271−272.
26. Schraml, M., Weber, A.; Gutser, R.; Schmidhalter, U. *Plant Nutrition for Food Security, Human Health and Environmental Protection*; Li, C. J. et al., Eds.; Tsinghua University Press: China, 2005; pp 1012−1013.
27. Michel, H. J.; Niclas, H. J.; Lang, B.; Wozniak, H.; Fuchs, M.; Zhang, Z. M.; Chen, G. X.. *Fertilization in the Third Millennium – Fertilizer, Food Security and Environmental Protection*; Lanzhu, J. I. et al., Eds.; Beijing, China, 2001; pp 1072−1079.
28. Khalil, M. I.; Buegger, F.; Schraml, M.; Gutser, R.; Richards, K. G.; Schmidhalter, U. *Soil Sci. Soc. Am. J.* **2009**, *73*, 1335–1344.

29. Khalil, M. I.; Schmidhalter, U.; Gutser, R. *J. Plant Nutr. Soil Sci.* **2009**, *172*, 651–660.
30. Zerulla, W.; Erhardt, K.; Pasda, G.; Dressel, J.; Barth, T.; Horchler von Locquenghien, K.; Raedle, M.; Leibold, E.; Wissemeier, A. *Biol. Fertil. Soils* **2001**, *34*, 79–84.
31. Tiessen, K. H. D.; Flaten, D. N.; Bullock, P. R.; Burton, D. L.; Grant, C. A.; Karamanos, R. E. *Agron. J.* **2006**, *98*, 1461–1470.
32. Hou, A. X.; Tsuruta, H. *Nutr. Cyclying Agroecosyst.* **2003**, *65*, 191–200.
33. Skiba, U.; Smith, K. A.; Fowler, D. *Soil Biol. Biochem.* **1993**, *25*, 1527–1536.
34. Delmas, R.; Serça, D.; Jambert, C. *Nutr. Cycling Agroecosyst.* **1997**, *48*, 51–60.
35. Hutchinson, G. L.; Brams, E. A. *J. Geophys. Res.* **1992**, *97*, 9889–9896.
36. Khalil, M. I.; Baggs, E. M. *Soil Biol. Biochem.* **2005**, *37*, 1785–1794.
37. Khalil, M. I.; Van Cleemput, O.; Rosenani, A. B.; Schmidhalter, U. *Commun. Soil Sci. Pl. Anal.* **2007**, *38*, 189–204.
38. IPCC. 2006. *IPCC Guidelines for national greenhouse gas 381 inventories - Volume 4: Agriculture, forestry and other land use*; URL: http://www.ipccnggip.iges.or.jp/public /2006gl/vol4.htm, 2006; pp 11.1−11.54.
39. Mosier, A. R.; Duxbury, J. M.; Freney, J. R.; Heinemeyer, O.; Minami, K. *Fertil. Res.* **1996**, *181*, 95–108.
40. McTaggart, I. P.; Clayton, H.; Parker, J.; Swan, L.; Smith, K. A. *Biol. Fertil. Soils* **1997**, *25*, 261–268.
41. Weiske, A.; Benckiser, G.; Herbert, T.; Ottow, J. C. G. *Biol. Fertil. Soils* **2001**, *34*, 109–117.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch009

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

Chapter 10

Mitigation Options for Methane and Nitrous Oxide from Agricultural Soil: From Field Measurement to Evaluation of Overall Effectiveness

Hiroko Akiyama,[*] Yoshitaka Uchida, and Akinori Yamamoto

National Institute for Agro-Environmental Sciences,
3-1-3 Kannondai, Tsukuba 305-8604, Japan
[*]E-mail: ahiroko@affrc.go.jp

This chapter describes field measurement techniques and mitigation options for methane (CH_4) and nitrous oxide (N_2O). Of the currently available technologies, the most potent and feasible options for mitigating CH_4 from paddy rice fields are mid-season drainage and off-season rice straw application (i.e., rice straw from a previous season is incorporated into the soil long before cultivation) and the use of nitrification inhibitors to mitigate N_2O emission from agricultural fields. Mid-season drainage and rice straw management were estimated to reduce global CH_4 emission by 16% each. If both of these mitigation options were adopted, the global CH_4 emission from rice paddies would be reduced by 30%. According to meta-analysis of field data, nitrification inhibitors significantly reduced N_2O emission from agricultural fields (mean effect: –38%) compared with that of conventional fertilizers.

Introduction

Agriculture is an important source of anthropogenic methane (CH_4) and nitrous oxide (N_2O). Rice cultivation is a major source of CH_4, which is a greenhouse gas. Yan et al. (*1*) estimated global CH_4 emission from rice paddy fields in 2000 as 25.6 Tg year^{-1}, which accounts for about 4% of global CH_4 emission. N_2O is a greenhouse gas, and is involved in the destruction of

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

stratospheric ozone. Agriculture is the largest single source of global N_2O. The agricultural sector is estimated to emit 2.8 Tg N $year^{-1}$ from soil and livestock, which accounts for 16% of global N_2O emission (42% of global anthropogenic N_2O emission) (*2*).

Recent advances in measurement techniques have led to significant improvements in the estimation of CH_4 and N_2O emission from agricultural fields. These advances are also expected to allow more accurate evaluations of existing mitigation options and to enhance the development of new mitigation technologies. Mitigation options for CH_4 and N_2O from agricultural soil have been intensively studied, primarily in field experiments. For example, 85 field measurements of the effectiveness of nitrification inhibitors on N_2O have been reported (*3*). Such field studies are useful for evaluating the effectiveness of mitigation options within local environments and for investigating the mechanisms of those mitigation options. However, CH_4 and N_2O fluxes and the effectiveness of mitigation options vary widely depending on environmental factors such as soil type and climate. Therefore, the overall effectiveness of mitigation options cannot be evaluated by a single field experiment. Statistical models and meta-analyses can combine the results of numerous field studies, and these statistical methods are useful for evaluating the overall effectiveness of mitigation options.

This chapter describes techniques for measuring CH_4 and N_2O fluxes and options for mitigating CH_4 and N_2O, focusing particularly on recent developments in the evaluation of the overall effectiveness of those mitigation options.

Estimating CH_4 and N_2O Fluxes from Agricultural Field

Field Measurement Techniques for CH_4 and N_2O Fluxes

There are two methods for measuring CH_4 and N_2O fluxes from soil: the use of closed chambers and micrometeorological techniques (*4*). In the closed chamber method, CH_4 and N_2O fluxes are determined by enclosing the atmosphere above soil and measuring the changes in headspace gas concentrations over time. This method is useful for comparisons between adjacent treatments and allows process-based studies. Rochette and Eriksen-Hamel (*5*) assessed chamber designs and techniques and made suggestions for obtaining more accurate flux measurements. Greenhouse gas fluxes from soils, and particularly those of N_2O, generally show large spatial and temporal variability. Therefore, to develop reasonable estimates of annual emission, it is important to monitor these fluxes from many chambers frequently over long periods. Because the manual chamber techniques are simple and inexpensive, it has become a widely used method. However, it is also labor-intensive and time-consuming. Consequently, flux measurements reported in the literatures have been typically obtained at intervals of 3 to 7 days over a period of several months (*6*). Automated chamber techniques reduce labor costs and achieve frequent and long-term sampling (these are described in the following section).

Micrometeorological (eddy covariance) techniques involve measurements of CH_4 and N_2O concentrations in the atmosphere at two or more points above the soil surface, in combination with meteorological measurements (e.g., wind speed, wind direction, and air temperature). These methods are suitable for measuring gas flux from a large area and are widely used to measure CO_2 fluxes from forests and agricultural fields. Although the eddy covariance technique has been used to measure CH_4 fluxes from a paddy rice field (*7*) and N_2O flux from a pasture (*8*), most studies of CH_4 and N_2O fluxes use chamber methods. One disadvantage of micrometeorological techniques is that they are less reliable at low wind speed and high atmospheric stability. In addition, because eddy covariance methods require large homogenous field sites, it is difficult to use them to evaluate mitigation options, which requires comparison among different treatments in adjacent field plots. Owing to these disadvantages, micrometeorological techniques are not discussed any further here.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

Automated Chamber Techniques

Automated chamber techniques were developed for frequent and long-term monitoring of gas fluxes, which is difficult with manual chamber methods. Since Schütz et al. (*9*) reported the use of an on-line connected automated sampling–analytical system (hereafter, an on-line monitoring system) for monitoring CH_4 fluxes from a rice field, various on-line systems for monitoring CH_4 and N_2O fluxes from soils have been developed (Figure 1) (*10–15*). These systems typically consist of automated chambers, a gas sampling system, and analytical systems such as a gas chromatograph or a photoacoustic infrared trace gas analyzer. Although on-line monitoring systems allow frequent and long-term flux measurement, one disadvantage is their large size. The monitoring systems can be difficult to transport between sites once they have been set up, and the analytical systems usually must be maintained at constant temperature. Because these systems also require frequent maintenance, field sites are usually limited to those near a research station that can provide appropriate maintenance facilities.

An alternative approach is the use of off-line monitoring systems, which are based on a gas sampling system with automated chambers. In such systems, the gas samples are transferred to a laboratory for analysis. Such systems greatly reduce the labor cost compared to that of manual chamber methods. In addition, the systems are much less expensive and smaller than typical on-line monitoring systems. Off-line monitoring systems are easier to transport between sites for subsequent experiments, and they can be set up in remote areas. Such systems using specially made aluminum gas tubes (*16*) or copper sample loops (*17*) as the sample gas containers were reported. Akiyama et al. (*18*) developed a simple and robust automated sampling system that uses common glass vials as the sample gas containers (Figure 2). Their system was further modified to control three chambers with one sampling unit and is commercially available in Japan. In 2010, more than 20 of these systems were in operation in Japan.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

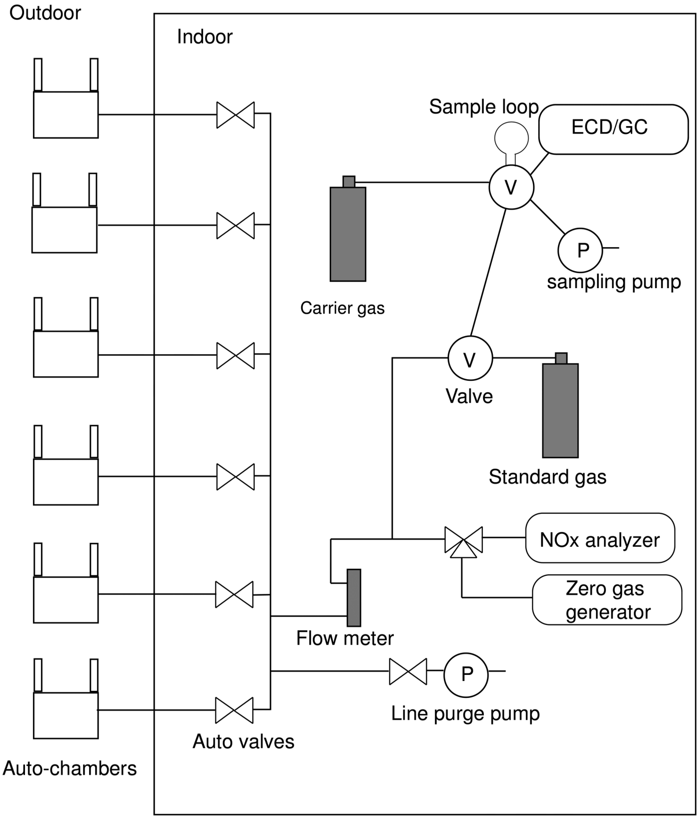

Outdoor
Indoor
Sample loop
ECD/GC
V
P
sampling pump
Carrier gas
V
Valve
Standard gas
NOx analyzer
Zero gas generator
Flow meter
P
Line purge pump
Auto valves
Auto-chambers

Figure 1. Example of an on-line connected automated sampling–analytical system. The system uses six auto-chambers. For N_2O and nitric oxide flux measurements, the lid of each chamber is closed to isolate the air inside from the atmosphere, and the air inside is drawn into the analysis system through a 10-m-long Teflon tube. GC-ECD: gas chromatograph equipped with electron capture detector. (Reproduced with permission from reference (10). Copyright 2000 Elsevier B.V.)

Mitigation Options for CH_4 Emission from Paddy Rice Fields

CH_4 is produced by the activity of CH_4-producing archaea (methanogens) as one of the terminal products in the anaerobic food web in rice paddy soils (*19*, *20*). Methanogens are strict anaerobes that require highly reducing conditions. Part of the produced CH_4 is consumed by CH_4-oxidizing bacteria (methanotrophs). The emission pathway of CH_4 accumulated in flooded paddy soils is as follows: diffusion into the flood water, loss through ebullition, and transport through the aerenchyma system of rice plants. In temperate rice fields, more than 90% of CH_4 is emitted via the plants (*21*). In tropical rice fields, however, the contribution of ebullition may be larger than in temperate regions (*22*). The possible strategies for mitigating CH_4 emission from rice cultivation include controlling the production, oxidation, or transport processes.

Yagi et al. (*19*) and Minamikawa et al. (*23*) assessed strategies for reducing CH_4 emission from paddy rice and reported various mitigation options, such as water management (mid-season drainage, short flooding period, and increased percolation), organic matter management (composting and off-season rice straw application), soil amendments (oxidants, soil dressing), no or minimum tillage, rotation, and the use of particular rice varieties. Among these, mid-season drainage and off-season rice straw application are the two most intensively studied technologies and therefore the most potent and feasible mitigation options.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

Water Management

Because CH_4 production occurs strictly under reducing conditions, water management greatly affects CH_4 emission from paddy rice fields. Mid-season drainage is a traditional management practice in which irrigated rice paddies are drained for 7-10 days during the growing season. Mid-season drainage is practiced in Japan, China, and other monsoon Asian countries to enhance grain yield, whereas continuous flooding of rice paddies is common in Vietnam (*1*). According to intensive field measurements across five countries (*24*), mid-season drainage reduces CH_4 emission by 7% to 80% compared to continuous flooding.

Another traditional water management practice of intermittent irrigation is also practiced in Japan, China, India and other Asian countries. In intermittent irrigation, drainage and irrigation repeated with few days cycle during the growing season. Studies have shown this practice to be effective for reducing CH_4 emission (*25–30*), although fewer studies have examined intermittent irrigation as compared to mid-season drainage. Lu et al. (*31*) reported that mid-season drainage reduced CH_4 emission by 44% compared to continuous flooding, and intermittent irrigation reduced CH_4 emission by 30% as compared with mid-season drainage. Yagi et al. (*32*) reported that a high percolation rate of irrigation water greatly reduced CH_4 emission, although there are not many reports related to this mitigation option.

Yan et al. (*33*) developed a statistical model using more than 1000 seasonal measurements from more than 100 sites. On the basis of their results, the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (*34*) adopted a 40% CH_4 reduction rate for a single mid-season drainage and 48% for drainage on multiple occasions, compared to continuous flooding (Figure 3). It should be noted that good irrigation systems are required to practice mid-season drainage or intermittent irrigation. In many parts of tropical Asia, rice fields are rain-fed, so they are naturally flooded during the monsoonal rainy season, making fully controlled drainage often impossible. For paddy fields in which irrigation water can be controlled, mid-season drainage would be one of most effective and cost-effective mitigation options.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

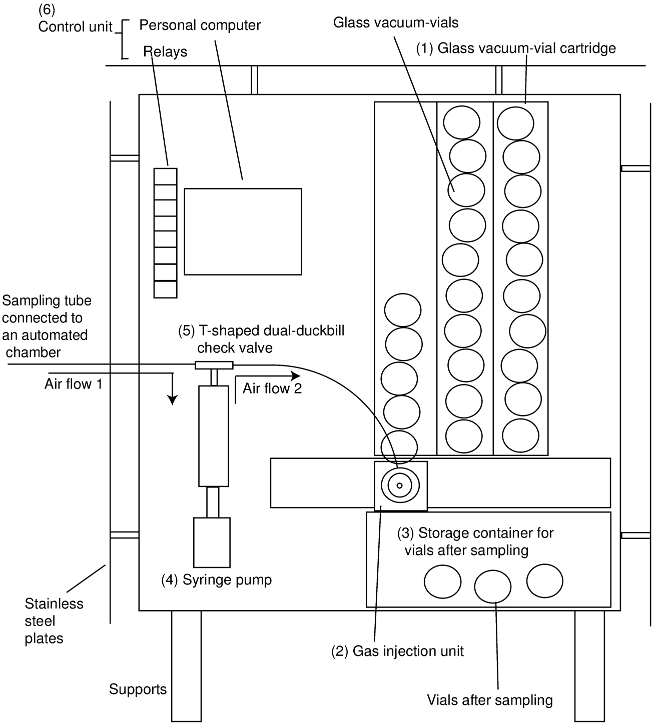

(6)
Control unit
Personal computer
Relays
Glass vacuum-vials
(1) Glass vacuum-vial cartridge
Sampling tube connected to an automated chamber
(5) T-shaped dual-duckbill check valve
Air flow 1
Air flow 2
(3) Storage container for vials after sampling
(4) Syringe pump
Stainless steel plates
(2) Gas injection unit
Supports
Vials after sampling

Figure 2. Schematic diagram of the automated gas sampling system (Japan patent pending 2008-011540). (Reproduced with permission from reference (18). Copyright 2009 John Wiley and Sons, Inc.)

Organic Matter Management

Rice straw, green manure and animal manure are widely applied in rice cultivation. This added organic matter acts as an electron donor and a substrate for CH_4 production. According to a statistical model developed by Yan et al. (*33*), the impact of organic amendments on CH_4 emission depends on the type and amount of material applied (Figure 4). When rice straw is applied during the off-season—that is, rice straw from a previous season is incorporated into the soil long before cultivation so that it decomposes under aerobic conditions—CH_4 emission is greatly reduced compared to application just before the cultivation. However, this practice is not universally applicable. For example, in double rice crop areas such as southern China, late rice is planted immediately after the early rice harvest, which necessitates that the rice straw be applied just before the growing season.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

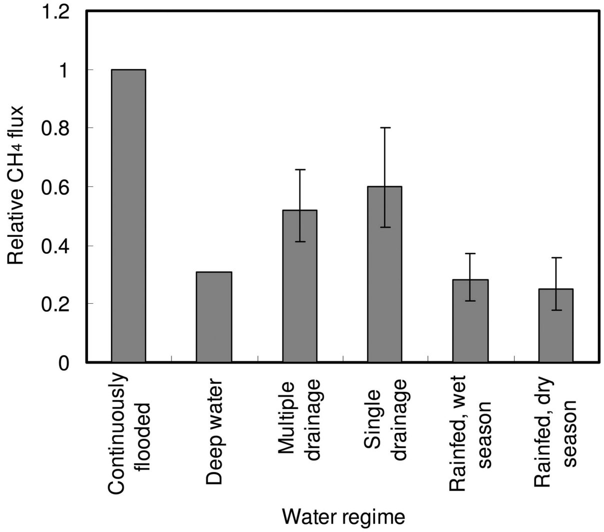


Figure 3. Relative CH_4 fluxes for different water regimes in the rice growing season, shown as relative fluxes (with flux from continuously flooded fields = 1), according to the statistical model of Yan et al. (33). Mean and 95% confidence intervals are shown. No confidence intervals are shown for deep water, because limited data were available. (Adapted with permission from reference (33). Copyright 2005 John Wiley and Sons, Inc.)

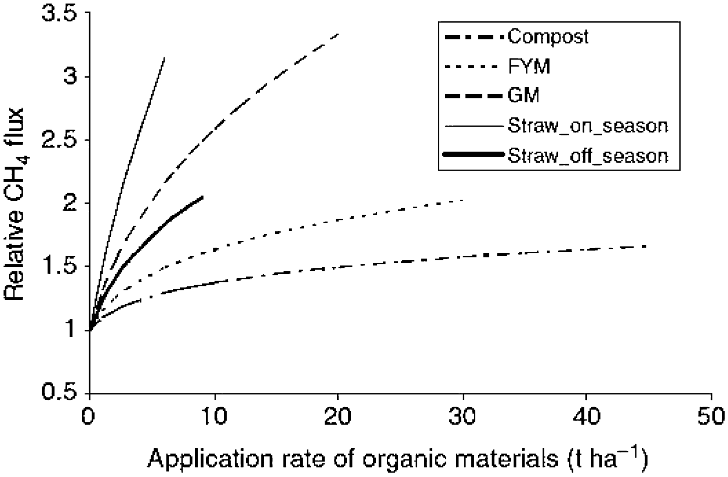


Figure 4. Simulated effects of different organic amendments on CH_4 emission from rice fields, assuming flux without any organic amendment to be 1. Note that straw is in dry weight but others are in fresh weight. FYM: farmyard manure; GM: green manure; Straw_on_season: rice straw applied just before planting; Straw_off_season: rice straw applied and incorporated long before planting. (Reproduced with permission from reference (33). Copyright 2005 John Wiley and Sons, Inc.)

The application of composted rice straw is more effective at reducing CH_4 emission than the use of non-composted straw (Figure 4). This practice, however, involves additional labor to transport material from and back to the field. If no straw is applied to the field, CH_4 emission is greatly reduced. In this case, however, rice straw is likely to be burned, which causes severe air pollution. Therefore, burning straw is prohibited in many places.

Other Options

Aside from reports on mid-season drainage and off-season straw application, there is little information available regarding other options for mitigating CH_4. The use of soil amendments, such as iron-containing materials, has been reported to be effective at reducing CH_4 emission by soil incubation or pot experiments (*35–37*) and field experiments (*38–40*). Although there are some reports that no-till is effective at reducing CH_4 emission (*41*, *42*), Ishibashi et al. (*43*) found that the mitigation effect of no-till declined over time and became ineffective after 4 to 7 years. Results of CH_4 emission reduction by planting certain rice varieties are conflicting, and Wassmann et al. (*44*) concluded that the variety-specific differences are small compared to the effects of other factors, and that they vary between seasons and are too elusive for accurate classification of varieties with respect to their CH_4 mitigation potential. Shiratori et al. (*45*) reported that tile drainage was effective at reducing CH_4 emission by oxidizing soil during the fallow season.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

The Mitigation Potential of Global CH_4 Emission from Paddy Fields

Yan et al. (*1*) investigated the global CH_4 mitigation potential of mid-season drainage and off-season rice straw application. They estimated that if all of the continuously flooded rice fields were drained at least once during the growing season, CH_4 emission would be reduced by 4.1 Tg year^{-1}, which is equal to a 16% reduction of global CH_4 emission from paddy fields. They estimated that off-season rice straw application (>30 days before cultivation) would result in a global reduction in CH_4 emission of 4.1 Tg year^{-1}. If both of these mitigation options were adopted, the global CH_4 emission from rice paddies could be reduced by 7.6 Tg year^{-1}, which is equal to a 30% reduction of global CH_4 emission from paddy rice fields.

Draining continuously flooded rice fields may lead to an increase in N_2O emission. However, Akiyama et al. (*46*) analyzed N_2O emission from paddy fields and concluded that the increase of global warming potential (GWP) resulting from the N_2O increase due to mid-season drainage is much smaller than the reduction in GWP that would result from the CH_4 reduction associated with draining the fields.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

Mitigation Options for N_2O Emission from Agricultural Fields

The application of nitrogen to soils as chemical or organic fertilizer stimulates N_2O production mainly via the biochemical processes of nitrification (under aerobic conditions) and denitrification (anaerobic conditions) (*47*). Nitrifier denitrification and the non-biochemical process of chemodenitrification are also involved in the production of N_2O in soil, although the contributions of these processes are unclear (*47*).

Optimizing Fertilizer Application Rate

The basic strategy for mitigating N_2O emission is optimizing nitrogen use efficiency (*48*), although this strategy has not been assessed quantitatively. Recently, Mosier et al. (*49*) introduced the concept of Greenhouse Gas Intensity, which is GWP divided by crop yield. By linking grain yield with greenhouse gas emission, it becomes possible to maximize yield in an environmentally sound manner by using appropriate levels of fertilizer-nitrogen input (*49*). Van Groenigen et al. (*50*) further developed this concept and conducted a meta-analysis of 147 field data from 19 studies. They found that optimizing fertilizer-nitrogen use efficiency under median rates of nitrogen input, rather than minimizing nitrogen application rates, resulted in minimum yield-scaled N_2O emission (i.e., N_2O emission in relation to aboveground nitrogen uptake) for non-leguminous arable crops. Yield-scaled N_2O emission was smallest (8.4 g N_2O-N kg^{-1} N uptake) at application rates of approximately 180–190 kg N ha^{-1} and increased sharply above that (e.g., 26.8 g N_2O-N kg^{-1} N uptake at 301 kg N ha^{-1}). If the aboveground nitrogen surplus was equal to or less than zero, yield-scaled N_2O emission remained stable and relatively small. At a nitrogen surplus of 90 kg N ha^{-1}, yield-scaled emission increased threefold. It is notable that minimum input of nitrogen fertilizer, which is generally considered to minimize N_2O emission, did not result in minimum N_2O emission when crop yield was taken into account. The strategies that reduce N_2O emission while maximizing nitrogen use efficiency will also reduce the environmental impacts caused by nitrogen fertilizer, such as nitrogen leaching and subsequent water pollution and ammonia volatilization.

Use of Enhanced-Efficiency Fertilizers

Enhanced-efficiency fertilizers, such as those containing nitrification and urease inhibitors and polymer-coated fertilizers, have been developed to increase the efficiency of fertilizer use by crops. Nitrification inhibitors are compounds that delay the oxidation of NH_4^+ by depressing the activities of nitrifiers in the soil, whereas urease inhibitors are compounds that delay the hydrolysis of urea. Polymer-coated fertilizers have a slower rate of nutrient release than conventional fertilizers. These types of enhanced-efficiency fertilizers have been studied intensively, and the findings indicate that they can be effective in increasing nitrogen use efficiency and have other benefits such as reducing labor and fuel costs (*51*) and decreasing nitrogen leaching (*52*). These technologies have not been used widely thus far, however, because a yield increase is rarely observed despite the additional costs (*53*, *54*).

Although many field studies have tested the effectiveness of enhanced-efficiency fertilizers on N_2O emission, the effectiveness of each option varies across sites depending on environmental factors and field management practices. Akiyama et al. (*3*) evaluated the overall effectiveness of enhanced-efficiency fertilizers on N_2O emission by a meta-analysis of field experiment data (113 datasets from 35 studies). The results showed that nitrification inhibitors significantly reduced N_2O emission (mean effect: –38%, Figure 5) compared with conventional fertilizers. Polymer-coated fertilizers also significantly reduced N_2O emission (–35%), whereas urease inhibitors were not effective at reducing N_2O. Nitrification inhibitors and polymer-coated fertilizers also significantly reduced nitric oxide emission (–46% and –40%, respectively). The effectiveness of nitrification inhibitors was relatively consistent across the various types of inhibitors and land uses. However, the effect of polymer-coated fertilizers showed contrasting results across soil and land-use types: they were significantly effective when used on imperfectly drained Gleysol grassland (–77%), but were ineffective when used on well-drained Andosol upland fields. Because the available data for polymer-coated fertilizers were dominated by certain regions and soil types, additional data are needed to evaluate their effectiveness more reliably.

Among nitrification inhibitors, dicyandiamide (DCD) has been the most widely tested. According to a meta-analysis of field experiments (*3*), DCD significantly reduces N_2O emission (mean effect: –30%) compared to conventional fertilizers. In contrast, a much larger effect of DCD (–61% to –76%) was reported based on soil column experiments (*55–58*). The reason for this discrepancy between field and laboratory experiments is that soil incubation or soil column experiments are often conducted under optimal conditions for DCD to inhibit nitrification (*4*).

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

Other Options

Bouwman et al. (*59*) estimated that replacing synthetic nitrogen fertilizer with animal manure nitrogen would result in a 33% reduction of global nitrogen fertilizer use and an 11% reduction of N_2O emission. In contrast, replacing synthetic nitrogen fertilizer with biological nitrogen fixation would lead to a N_2O increase at the global scale (*59*).

Many studies have suggested that no-till and reduced tillage can decrease agriculture's contribution to greenhouse gas emission through carbon sequestration (*60*). However, conclusions on the effect of these practices on greenhouse gas budgets are complicated by the inconsistent effects of no-till and reduced tillage on N_2O emission (*60*, *61*). Rochette (*61*) summarized available data from field studies and concluded that no-till generally increased N_2O emission in poorly aerated soils but had a neutral effect in soils with good and medium aeration. Six et al. (*60*) summarized field experiment data from humid and dry temperate climates and concluded that mitigation of GWP by the adoption of no-till is variable and complex.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

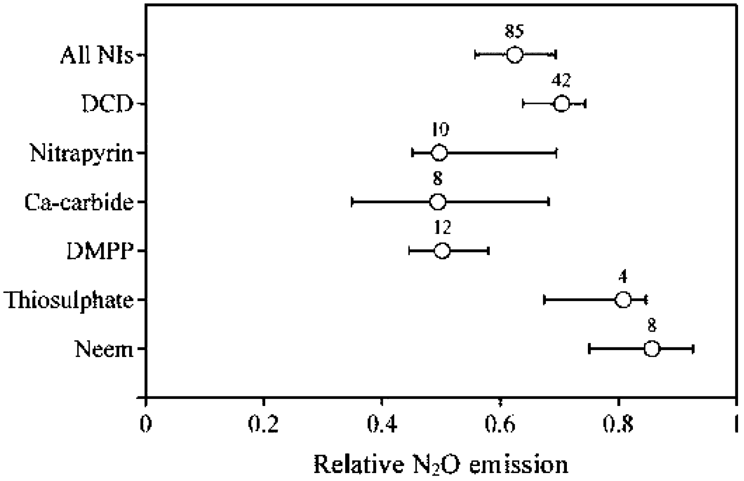


Figure 5. The effect of nitrification inhibitors (NIs) on N_2O emission, shown as relative emission (N_2O emission from conventional fertilizer = 1), by a meta-analysis of field experiments. Mean effect and 95% confidence intervals are shown. Numerals indicate number of observations. (Note that the sum of observations for each type of NI does not match the number of observations for all NIs because one dataset that tested 2-amino-4-chloro-6-methyl pyrimidine is included in the all NIs category.) All NIs: integrated effect of all types of NI; DCD: dicyandiamide; DMPP: 3,4-dimethyl pyrazole phosphate; Ca-carbide: encapsulated and coated calcium carbide; Neem: various products such as neem oil–coated urea, neem-coated urea, nimin-coated urea, and urea with neem cake from the Indian neem tree (Azadirachta indica). (Reproduced with permission from reference (3). Copyright 2010 John Wiley and Sons, Inc.)

Conclusions

Recent advances in measurement techniques, such as the use of automated chambers, have made significant improvements in the estimation of CH_4 and N_2O emission from agricultural fields. These advances are also expected to allow more accurate evaluation of existing mitigation options and the development of new mitigation technologies.

Of the currently available mitigation technologies, the most potent and feasible mitigation options are mid-season drainage and off-season rice straw application for CH_4 from paddy rice fields and nitrification inhibitors for N_2O from agricultural fields. Mid-season drainage and rice straw management is estimated to reduce global CH_4 emission by 16% each. If both of these mitigation options were adopted, the global CH_4 emission from rice paddies could be reduced by 30%. According to meta-analysis of field data, nitrification inhibitors significantly reduce N_2O emission from agricultural fields (mean effect: –38%) compared with that of conventional fertilizers. Optimizing fertilizer-nitrogen use efficiency under median rates of nitrogen input would minimize yield-scaled N_2O

emission. The strategies that reduce N_2O emission while maximizing nitrogen use efficiency will also reduce the environmental impacts caused by nitrogen fertilizer, such as nitrogen leaching and subsequent water pollution and ammonia volatilization.

References

1. Yan, X.; Akiyama, H.; Yagi, K.; Akimoto, H. *Global Biogeochem. Cycles* **2009**, *23*. doi.10.1029/2008GB003299.
2. Denman, K. L.; Brasseur, G.; Chidthaisong, A.; Ciais, P.; Cox, P. M.; Dickinson, R. E.; Hauglustaine, D.; Heinze, C.; Holland, E.; Jacob, D.; Lohmann, U.; Ramachandran, S.; da Silva Dias, P. L.; Wofsy S. C.; Zhang, X. In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press: Cambridge, U.K., 2007; pp 500–587.
3. Akiyama, H.; Yan, X.; Yagi, K. *Global Change Biol.* **2010**, *16*, 1837–1846.
4. de Klein, C. A. M.; van der Weerden T. J.; Eckard R. J. In *Nitrous Oxide and Climate Change*; Smith, K., Ed.; Earthscan: London, 2010; pp 107–142.
5. Rochette, P.; Eriksen-Hamel, N. S. *Soil Sci. Soc. Am. J.* **2008**, *72* (2), 331–342.
6. Bouwman, A. F.; Boumans, L. J. M.; Batjes N. H. *Global Biogeochem. Cycles* **2002**, *16(4)*, GB1058, doi:10.1029/2001GB001811.
7. Miyata, A.; Iwata, T.; Nagai, H.; Yamada, T.; Yoshikoshi, H.; Mano, M.; Ono, K.; Han, G. H.; Harazono, Y.; Ohtaki, E.; Baten, M. A.; Inohara, S.; Takimoto, T.; Saito, M. *Phyton-Ann. Rei Bot.* **2005**, *45* (4), 89–97.
8. Phillips, F. A.; Leuning, R.; Baigenta, R.; Kelly, K. B.; Denmead, O. T. *Agric. For. Meteorol.* **2007**, *143* (1–2), 92–105.
9. Schütz, H.; Holzapfelpschorn, A.; Conrad, R.; Rennenberg, H.; Seiler, W. *J. Geophys. Res. Atmos.* **1989**, *94* (D13), 16405–16416.
10. Akiyama, H.; Tsuruta, H.; Watanabe, T. *Chemosphere: Global Change Sci.* **2000**, *2* (3–4), 313–320.
11. Ambus, P.; Robertson, G. P. *Soil Sci. Soci. Am. J.* **1998**, *62* (2), 394–400.
12. Loftfield, N. S.; Brumme, R.; Beese, F. *Soil Sci. Soc. Am. J.* **1992**, *56* (4), 1147–1150.
13. Nishimura, S.; Sudo, S.; Akiyama, H.; Yonemura, S.; Yagi, K.; Tsuruta, H. *Soil Sci. Plant Nutr.* **2005**, *51* (4), 557–564.
14. Thornton, F. C.; Valente, R. J. *Soil Sci. Soc. Am. J.* **1996**, *60* (4), 1127–1133.
15. Yamulki, S.; Jarvis, S. C. *J. Geophys. Res. Atmos.* **1999**, *104* (D5), 5463–5469.
16. Scott, A.; Crichton, I.; Ball, B. C. *J. Environ. Qual.* **1999**, *28* (5), 1637–1643.
17. Smith, K. A.; Dobbie, K. E. *Global Change Biol.* **2001**, *7* (8), 933–945.
18. Akiyama, H.; Hayakawa, A.; Sudo, S.; Yonemura, S.; Tanonaka, T.; Yagi, K. *Soil Sci. Plant Nutr.* **2009**, *55* (3), 435–440.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

19. Yagi, K.; Tsuruta, H.; Minami, K. *Nutri. Cycling Agroecosyst.* **1997**, *49* (1–3), 213–220.
20. Conen, F.; Smith, K. A.; Yagi, K. In *Methane and Climate Change*; Reay, D., Smith, P., van Amstel, A., Eds.; Earthscan: London, 2010; pp 115–135.
21. Schutz, H.; Seiler, W.; Conrad, R. *Biogeochemistry* **1989**, *7* (1), 33–53.
22. Vandergon, H.; Neue, H. U. *Global Biogeochem. Cycles* **1995**, *9* (1), 11–22.
23. Minamikawa, K.; Sakai, N.; Yagi, K. *Microbes Environ.* **2006**, *21* (3), 135–147.
24. Wassmann, R.; Lantin, R. S.; Neue, H. U.; Buendia, L. V.; Corton, T. M.; Lu, Y. *Nutr. Cycling Agroecosyst.* **2000**, *58* (1–3), 23–36.
25. Adhya, T. K.; Bharati, K.; Mohanty, S. R.; Ramakrishnan, B.; Rao, V. R.; Sethunathan, N.; Wassmann, R. *Nutr. Cyclying Agroecosyst.* **2000**, *58* (1–3), 95–105.
26. Jain, M. C.; Kumar, S.; Wassmann, R.; Mitra, S.; Singh, S. D.; Singh, J. P.; Singh, R.; Yadav, A. K.; Gupta, S. *Nutr. Cyclying Agroecosyst.* **2000**, *58* (1–3), 75–83.
27. Yang, S. S.; Chang, H. L. *Biol. Fertil. Soils* **2001**, *33* (2), 157–165.
28. Pathak, H.; Prasad, S.; Bhatia, A.; Singh, S.; Kumar, S.; Singh, J.; Jain, M. C. *Agric., Ecosyst. Environ.* **2003**, *97* (1–3), 309–316.
29. Yue, J.; Shi, Y.; Liang, W.; Wu, J.; Wang, C. R.; Huang, G. H. *Nutr. Cycling Agroecosyst.* **2005**, *73* (2–3), 293–301.
30. Jiao, Z. H.; Hou, A. X.; Shi, Y.; Huang, G. H.; Wang, Y. H.; Chen, X. *Commun. Soil Sci. Plant Anal.* **2006**, *37* (13–14), 1889–1903.
31. Lu, W. F.; Chen, W.; Duan, B. W.; Guo, W. M.; Lu, Y.; Lantin, R. S.; Wassmann, R.; Neue, H. U. *Nutr. Cycling Agroecosyst.* **2000**, *58* (1–3), 65–73.
32. Yagi, K.; Minami, K.; Ogawa, Y. *Plant Soil* **1998**, *198* (2), 193–200.
33. Yan, X. Y.; Yagi, K.; Akiyama, H.; Akimoto, H. *Global Change Biol.* **2005**, *11* (7), 1131–1141.
34. IPCC, *2006 IPCC Guidelines for National Greenhouse Gas Inventories, Volume 4 Agriculture, Forestry and Other Land Use*; Institute for Global Environmental Strategies (IGES): Hayama, Japan, 2006.
35. Furukawa, Y.; Inubushi, K. *Soil Sci. Plant Nutr.* **2004**, *50* (7), 1029–1036.
36. Qu, D.; Ratering, S.; Schnell, S. *Bull. Environ. Contam. Toxicol.* **2004**, *72* (6), 1172–1181.
37. Ali, M. A.; Lee, C. H.; Kim, S. Y.; Kim, P. J. *Waste Manage.* **2009**, *29* (10), 2759–2764.
38. Jackel, U.; Russo, S.; Schnell, S. *Soil Biol. Biochem.* **2005**, *37* (11), 2150–2154.
39. Mukherjee, R.; Barua, A.; Sarkar, U.; De, B. K.; Mandal, A. K. *Int. J. Greenhouse Gas Control* **2009**, *3* (5), 664–672.
40. Ali, M. A.; Lee, C. H.; Lee, Y. B.; Kim, P. J. *Agric., Ecosyst. Environ.* **2009**, *132* (1–2), 16–22.
41. Chareonsilp, N.; Buddhaboon, C.; Promnart, P.; Wassmann, R.; Lantin, R. S. *Nutri. Cycl. Agroecosys.* **2000**, *58* (1–3), 121–130.
42. Ahmad, S.; Li, C. F.; Dai, G. Z.; Zhan, M.; Wang, J. P.; Pan, S. G.; Cao, C. G. *Soil Tillage Res.* **2009**, *106* (1), 54–61.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch010

43. Ishibashi, E.; Akai, N.; Ohya, M.; Ishii, T.; Tsuruta H. *Japanese Soil Sic. Plant Nutri.* 2001**,** *72,* 542–549 (In Japanese with English abstract).
44. Wassmann, R.; Aulakh, M. S.; Lantin, R. S.; Rennenberg, H.; Aduna, J. B. *Nutri. Cycling Agroecosyst.* **2002**, *64* (1–2), 111–124.
45. Shiratori, Y.; Watanabe, H; Furukawa, Y.; Tsuruta, H; Inubushi, K. *Soil Sci. Plant Nutr.* **2007**, *53* (4), 387–400.
46. Akiyama, H.; Yagi K.; Yan X. Y. *Global Biogeochem. Cycles* **2005**, *19(1)*, GB1005, doi:10.1029/2004GB002378.
47. Baggs E. M.; Philippot, L. In *Nitrous Oxide and Climate Change*; Smith, K. A., Ed.; Earthscan: London, U.K.; pp 4–35.
48. Saggar, S.; Tate, K. R.; Giltrap, D. L.; Singh, J. *Plant Soil* **2008**, *309* (1–2), 25–42.
49. Mosier, A. R.; Halvorson, A. D.; Reule, C. A.; Liu, X. J. J. *J. Environ. Qual.* **2006**, *35* (4), 1584–1598.
50. van Groenigen, J. W.; Velthof, G. L.; Oenema, O.; Van Groenigen, K. J.; van Kessel, C. *European J. Soil Sci.* **2010**, *61* (6), 903–913.
51. Grant, C. IFA International Workshop on Enhanced-Efficiency Fertilizers, Frankfurt, Germany, 2005, URL http://www.fertilizer.org/ifa/Home-Page/LIBRARY/Conference-proceedings/Agriculture-Conferences/2005-IFA-Agriculture-Workshop.
52. Bolan, N. S.; Saggar, S.; Luo, J. F.; Bhandral, R.; Singh, J. *Adv. Agron.* **2004**, *84*, 37–120.
53. Frye, W. IFA International Workshop on Enhanced-Efficiency Fertilizers, Frankfurt, Germany, 2005, URL http://www.fertilizer.org/ifa/Home-Page/LIBRARY/Conference-proceedings/Agriculture-Conferences/2005-IFA-Agriculture-Workshop.
54. Guertal, E. A. *HortTechnology* **2009**, *19* (1), 16–19.
55. Di, H.; Cameron, K.; Sherlock, R.; Shen, J. P.; He, J. Z.; Winefield, C. *J. Soils Sediments* **2010**, *10* (5), 943–954.
56. Di, H. J.; Cameron, K. C. *Soil Use Management* **2003**, *19* (4), 284–290.
57. Di, H. J.; Cameron, K. C. *Biol. Fertil. Soils* **2006**, *42* (6), 472–480.
58. Di, H. J.; Cameron, K. C.; Sherlock, R. R. *Soil Use Manage.* **2007**, *23* (1), 1–9.
59. Bouwman, A. F.; Stehfest, E.; van Kessel, C. In *Nitrous oxide and Climate Change*; Smith, K. A., Ed.; Earthscan: London, 2010; pp 85–106.
60. Six, J.; Ogle, S. M.; Breidt, F. J.; Conant, R. T.; Mosier, A. R.; Paustian, K. *Global Change Biol.* **2004**, *10* (2), 155–160.
61. Rochette, P. *Soil Tillage Res.* **2008**, *101* (1–2), 97–100.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Chapter 11

Effects of Nitrogen Fertilizer Types on Nitrous Oxide Emissions

Martin Burger*,[1] **and Rodney T. Venterea**[2]

[1]**University of California Davis, Dept. of Land, Air & Water Resources,**
1 Shields Ave., Davis, CA 95616
[2]**USDA-ARS, Soil and Water Management Unit, 1991 Upper Buford Circle,**
St. Paul, MN 55108
***E-mail: mburger@ucdavis.edu**

The factors controlling nitrous oxide (N_2O) emissions after fertilizer nitrogen (N) applications are well studied. This information can be used to choose appropriate fertilizer sources and placement methods in order to minimize direct fertilizer-induced N_2O emissions in cropping systems. Several field experiments have shown that locally concentrated, alkaline-forming fertilizers, such as anhydrous ammonia or subsurface banded urea, in soil produce more N_2O than evenly dispersed fertilizers. Nitrification inhibitors lower N_2O emissions, but fertilizers employing a physical barrier to control the release of plant-available N are not always effective in this respect. Adding the global warming potential from fertilizer production and field application can shift the overall greenhouse gas emissions among fertility practices depending on the fertilizer type being used. The research findings presented in this review and greater knowledge about the pathways of N_2O production will aid in providing better informed choices of N source and placement method in cropping systems.

Introduction

There is little doubt that increasing food production for the growing human population is the underlying cause of rising atmospheric N_2O concentration (*1*–*3*). Increased N fertilizer use and N re-concentrating processes, such as

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

manure production, are driving the increase in atmospheric N_2O (*3*). Nitrogen fertilizer is a key input to sustain crop yields, but many studies have shown that microbial production of N_2O in soil is stimulated by fertilizer N inputs (*2*, *4–8*). Other undesirable consequences of fertilizer N applications include ammonia (NH_3) volatilization and nitric oxide (NO) emissions, each of which can cause N deposition and increases in reactive N in the environment, and nitrate (NO_3^-) leaching, which has the potential to negatively affect ground- and surface waters on a regional basis (*9*). The proportion of N losses that initially occur in the form of NH_3, NO or NO_3 and are eventually converted to N_2O (*1–3*) is difficult to ascertain with measurements because many complex factors regulate the transformation of these N species once they leave the fertilized field. However, direct fertilizer-induced N_2O emissions have been measured in many studies that have provided much information about factors controlling N_2O emissions after fertilizer N applications. This information can be used to select the most appropriate N fertilizer and application practice in a given edaphic, climatic and agronomic situation in order to keep direct N_2O emissions as low as possible. Soil water content, by its regulation of oxygen (O_2) diffusion and microbial activity, carbon (C) availability, temperature, pH, abundance and diversity of N cycling bacteria (*10*), and ammonium (NH_4^+) and nitrate (NO_3^-) concentrations are the main factors that interact to control the abundance and the pathways of N_2O production and emission to the atmosphere (*11–13*). In addition to climate, soil texture, drainage, and organic C, management practices, such as cropping sequence, tillage, irrigation technique, fertilizer type, application rate, placement, and timing of application influence the direct emissions from fertilizer N amendments (*4*).

In an initial meta-analysis comprising 846 data sets (*6*), fertilizer type was found to significantly affect N_2O emissions. Anhydrous ammonia (AA) and aqueous ammonia produced the highest and certain ammonium-based (ammonium bicarbonate, ammonium chloride, ammonium sulfate, ammonium phosphate) fertilizers the lowest mean N_2O emissions, i.e. 4.0 and 1.2 to 1.4 kg N_2O-N ha^{-1} during the experiment period, respectively (*6*). [About one half of the summarized experiments lasted <120 d. The N_2O emissions values included background N_2O emissions.] According to the same meta-analysis, urea (U; 1.7 kg N2O-N ha^{-1}), calcium nitrate, potassium nitrate, and sodium nitrate (2.0 kg N_2O-N ha^{-1}), ammonium nitrate (2.7 kg N_2O-N ha^{-1}), and urea ammonium nitrate (UAN; 2.8 kg N_2O-N ha^{-1}) resulted in intermediate emissions. However, in an extended and updated study (*8*), which included >1000 data sets, most differences in emissions due to fertilizer types disappeared when all significant factors (e.g. application rate, climate, soil organic C, cropping system) were taken into account for the assessment of fertilizer type impact alone (*8*). Comparing fertilizer source effects *via* meta-analyses is problematic because of the varied amounts of N applied, the differences of cropping systems and soil types, length of sampling periods, climatic conditions, and interactions among these factors in the different experiments (*4*).

To date, relatively few studies have been conducted in which the effect of fertilizer type on N_2O emissions has been evaluated in side-by-side experiments. However, there is a large body of knowledge about N transformations in soil and how synthetic fertilizers affect soil chemistry that can be used to develop best management practices that minimize N_2O emissions without sacrificing yields. In this chapter, the pathways of N_2O production and N fertilizer effects on the soil environment, as well as field measurements of N_2O emissions after applications of different fertilizer sources, including controlled release fertilizers, and greenhouse gas emissions from fertilizer production are reviewed with the goal of identifying areas that need additional investigation and those offering the best mitigation opportunities.

Pathways of N_2O Production

Microbiological Production

In soil, N_2O is produced during the processes of nitrification and denitrification *via* multiple specific pathways. Nitrous oxide is an obligate intermediate during denitrification, the dissimilatory reduction of NO_3^- or nitrite (NO_2^-) to nitric oxide (NO), to N_2O and then to dinitrogen (N_2), concomitant with energy conservation. Denitrification occurs under anaerobic conditions and is performed by facultative heterotrophic bacteria, which can be grouped as either complete or incomplete denitrifiers based on their ability to produce N_2 or N_2O as an end product, respectively (*14*). Some fungi have also been shown to produce N_2O during dissimilatory reduction of NO_2^- and NO_3^- (*15*).

Nitrification is the microbial oxidation of NH_3 or ammonium (NH_4^+) to NO_2^- and then to NO_3^-. Oxidation of NH_3 is catalyzed by the enzyme ammonia monooxygenase (AMO) to form hydroxylamine (NH_2OH). The enzyme hydroxylamine oxidoreductase catalyzes the oxidation of NH_2OH to NO_2^-. Incomplete oxidation of NH_2OH in the presence of manganese(II) (*18*) and chemical decomposition of NH_2OH may produce N_2O (*19*, *20*). Hydroxylamine rarely builds up in soil, possibly because electrons needed to sustain ammonia oxidation are obtained from the oxidation of NH_2OH to NO_2^- (*13*, *21*) and because at high concentrations NH_2OH is toxic to nitrifiers (*22*). There is evidence that N_2O production from NH_2OH is somewhat enhanced when both NH_2OH and NO_2^- are added to soil due to a possible interaction of NH_2OH with NO_2^- (*23*).

The first step of nitrification (NH_3 to NO_2^-) is carried out by one group of microorganisms, e.g. *Nitrosomonas* spp., while a separate type of microorganism, e.g. *Nitrobacter* spp., carries out the oxidation of NO_2^- to NO_3^-. Most nitrifying bacteria are chemoautotrophs that derive energy from the oxidation of NH_3, or NO_2^-, and use carbon dioxide (CO_2) as their C source and O_2 as electron acceptor. However, some ammonia oxidizers (*Nitrosomonas europaea, Nitrosolobus* spp., *Nitrosospira* spp., *Nitrosococcus* spp.) are capable of reducing NO_2^- to N_2O under aerobic and O_2-limited conditions (*24–26*) in a process that is sometimes referred to as "nitrifier-denitrification". A heterotrophic pathway of nitrification is also known to produce N_2O via reduction of NO_2^- in low-O_2 soil environments (*27*).

Evidence that substantial N_2O fluxes must be attributed to nitrification was presented several decades ago (*16*, *17*). Nitrous oxide production during nitrification has since been studied in detail by many researchers (*13*, *28–32*). Quantitatively distinguishing between N_2O produced via NH_2OH

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

oxidation,nitrifier-denitrification, or coupled nitrification-denitrification (involving oxidation of NO_2^- and subsequent reduction of NO_3^-) has only recently become possible in controlled laboratory settings (*30*, *32–34*).

Abiotic Production

Nitrous oxide may also form from NO_2^- *via* so-called chemodenitrification involving reactions with metallic cations and/or organic matter (*13*, *22*, *35–39*). This process requires the biological production of NO_2^-, usually via nitrification, followed by chemical reactions that can produce NO and/or N_2O. Thus, it cannot be classified as strictly abiotic but more accurately as a biotic-abiotic reaction sequence. Early studies showed that N_2O is chemically produced following NO_2^- addition to acidic soil organic matter fractions (*40*) and under neutral to slightly acidic conditions more representative of soil (*38*). Reaction pathways proposed in earlier studies have been partly confirmed using ^{15}N nuclear magnetic resonance (*39*) although there has been relatively little work done recently to test reaction pathways proposed in early studies. The kinetics of N_2O production via reaction of NO_2^- with whole soils were recently characterized under conditions of varying O_2 availability (*29*). This study indicated that, in the presence of measurable amounts of soil NO_2^-, the proportion of N_2O produced from chemodenitrification under fully aerobic conditions ranged from 37 to 87 %, with the remainder attributable to biological processes (most likely nitrifier-denitrification). As O_2 availability decreased, the proportion of biological production increased. These results highlight the challenge of elucidating mechanisms of N_2O production in soil given the fact that multiple processes can occur simultaneously even within a relatively small soil volume. While recent advances in isotopic techniques have attempted to distinguish N_2O produced during specific microbial processes, as yet these techniques do not currently account for all potential reactions (e.g. chemodentrification) (*41*, *42*).

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Nitrogen Fertilizer Effects on Soil pH and N Transformations

Fertilizers influence N_2O emissions through their effects on soil pH. Most synthetic N fertilizers are ammonia based. Both in the short term (days to weeks) and long term (weeks to years), application of ammonium fertilizers generate soil acidity through nitrification (*43–45*). Soil acidity can increase N_2O emissions during denitrification by increasing the $N_2O/(N_2O+N_2)$ product ratio after additions of NO_3^- (*44*, *46–48*). The increase of this ratio, which is more pronounced at low pH (<6.0), has been explained by differences in the affinity of the enzymes nitrate reductase and nitrous oxide reductase for NO_3^- and N_2O, respectively (*49*). In the short term, some fertilizers, such as ammonium sulfate $(NH_4)_2SO_4)$, ammonium nitrate (NH_4NO_3), and mono-ammonium phosphate ($NH_4H_2PO_4$) have the potential to immediately acidify the soil (*44*, *45*). Thus, it could be expected that additions of $NH_4NO_3^-$ would enhance N_2O emissions under denitrifying conditions, especially in acidic soils. In laboratory incubations of water logged soils that had previously, under aerobic conditions, received acidifying N fertilizers, the proportion of $N_2O/(N_2O+N_2)$ emitted was in the short term indeed higher than for soils previously incubated with alkaline-forming fertilizers (*44*).

Applications of U, AA, and di-ammonium phosphate ($(NH_4)_2HPO_4$) will initially increase the soil pH (*44*, *45*). After application of AA, the rise in pH occurs immediately. Urea hydrolyzes within days to NH_3 and CO_2 in the presence of the enzyme urease and a small amount of moisture. Urease activity increases with increasing soil pH and peaks at a pH of 6.0 to 6.5 (*50*, *51*). The effect of pH on urease activity is more pronounced at higher substrate concentrations (*50*). Urease is ubiquitous in surface soil, on plants and biomass residue and manure (*52*). The increase in pH after AA or U application can be in the range of 2 pH units in some soils and last up to 10 days (*44*, *53*). The increase in pH is generally greater for AA than for U because after hydrolysis of U not all the CO_2 escapes immediately to the atmosphere. After the initial period of increased soil pH following AA application, once nitrification begins to proceed, soil pH can also decrease over a period of days to weeks and return to pre-application levels or below (*37*, *53*). Thus, the net effect of alkaline-forming fertilizers on pH-related impacts on N_2O emissions may be difficult to predict.

Nitrification rates are generally higher for alkaline-forming than for acidifying N fertilizers (*44*, *45*, *54*). One of the consequences of applying alkaline-forming fertilizers in concentrated form is the accumulation of NO_2^-, which is likely the main substrate for N_2O production during nitrification (*13*, *29*). The accumulation of NO_2^- after applications of AA or U was reported several decades ago (*45*, *55*, *56*) and has since been observed by many researchers (*20*, *53*, *54*, *57*). Although nitrification generally lowers the soil pH of alkaline-forming fertilizers after 1 to 2 weeks, NO_2^- may be present for longer periods. High concentrations of NO_2^- (>20 mg NO_2^- N kg^{-1}) have been detected several months after fall injection of AA and urea application in a range of soils (*55*, *56*). The presence of NO_2^- could also stimulate N_2O emissions under denitrifying conditions as NO_2^- has been shown to increase the $N_2O/(N_2O+N_2)$ product ratio even more than NO_3^- additions (*47*, *58*, *59*).

Nitrite probably accumulates after applications of AA or U because *Nitrobacter* spp., which carries out the second step of nitrification (NO_2^- to NO_3^-), is inhibited under these conditions. Rising NH_3 levels have often been assumed to be more toxic to *Nitrobacter* spp. than to *Nitrosomonas* spp. (*35*, *60*) notwithstanding that high concentrations of NH_3 seem to slow down its oxidation (*61*). However, in controlled experiments in bench scale nitrification reactors, the increase in pH to levels between 7.8 to 8.5 and high ammonia oxidizer activity, assessed by respirometry, were identified as inhibitory to *Nitrobacter* spp. activity, and this was confirmed by *Nitrobacter* spp. ribosomal RNA transcript abundance, whereas changes in NH_3 concentration had no effect on *Nitrobacter* spp. activity (*62*).

Alkaline-forming fertilizers can stimulate denitrification under anaerobic conditions by increasing the solubility of soil organic matter (*63*) because denitrification is often controlled by the amount of oxidizable C in soil, especially when NO_3^- availability is not limited (*12*, *64*). Laboratory and field studies (*44*, *65*) indicated that AA, which usually increases the soil pH more than U,

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

lead to a greater increase of dissolved organic C (DOC) than U. However, the effect of DOC on N_2O emissions after applications of alkaline-forming fertilizers is difficult to ascertain without better knowledge about the contribution of nitrification and denitrification to total N_2O flux.

Fertilizer Placement Effects on N Transformations

Concentrating nitrifiable fertilizers increases the potential for NO_2^- formation and N_2O production. The relationships among ammoniacal N concentration, soil pH and the influence of N fertilizers on the pH in the fertilizers' immediate vicinity (acid- or alkaline-forming) determine the extent of NO_2^- accumulation, with possible implications for N_2O losses. Hauck and Stephens (*45*) concluded that large granules, high N application rates (>50 μg N g^{-1} soil), low soil buffer capacity, as well as alkaline-forming N fertilizers lead to NO_2^- accumulation and that the concentration effect of nitrifiable fertilizers on NO_2^- accumulation is more pronounced in calcareous soils.

Increasing U concentration in the soil, e.g. by the granule size, from powder to prills to super granule, or by placement, from broadcasting to banding to nest application, decreases NH_4^+ oxidation rates (*61*), increases NO_2^- concentration, and increases N_2O production (*20*, *57*). In a 45-d incubation experiment, total N_2O production increased with U granule size (<2 to 13 mm) ranging from 0.2 to 0.6% of the added N in sandy and silt loam and up to 2.6% in a clay loam soil at field capacity (*66*). In the same experiment, NH_3 volatilization decreased with increasing granule size.

Few field studies have evaluated the effect of U placement method on N_2O emissions. Drilling U almost doubled N_2O emissions compared to broadcast application in rice (*Oryza sativa* L.) fields (*57*, *67*, *68*). Placing 100 kg urea-N ha^{-1} in nests 5 cm below the surface resulted in almost three times higher N_2O emissions (0.57% of the applied N) than broadcasting (0.21%), whereas banding U at 5 cm depth increased the emissions to 0.28% in silt-loam soil in a canola (*Brassica rapa* L.) system in MT, U.S.A. (*57*). Banding U 10 cm below the soil surface in a silt loam soil lead to relatively high seasonal N_2O-N losses of 3.8% of the applied urea-N (*69*). Concentrating U in bands or nests improves N recovery by the crop (*61*), which has been attributed mainly to slower nitrification. However, concentrating ammonia fertilizers increases the potential for N_2O production.

The effects of fertilizer application depth on N_2O emissions may depend on tillage practices, which can affect soil water conditions and vertical distribution of C availability. Seasonal N_2O emissions were significantly lower under no-till than conventional tillage after injection of AA at 15-20 cm depth in a corn (*Zea mays* L.)-soybean [*Glycine max* (L.) Merr.] system, which was attributed to greater abundance of facultative denitrifier populations in the conventionally tilled soil, presumably due to moldboard plowing, at the depth where the fertilizer was placed (*70*). In contrast, N_2O emissions after broadcast urea application in the same experiment were significantly higher under no-till than conventional tillage, but only half as high as in the AA treated plots. Lower N_2O emissions were observed after placement of NH_4NO_3 side-dress fertilizer at 2 cm than with N placement at 10 cm depth in a fine-textured clay loam soil in a wheat (*Triticum aestivum* L.) system in Eastern Canada (*71*). Zone-tillage had the lowest and conventional tillage the highest cumulative N_2O emissions. In this case, the differences in N_2O emissions were attributed mainly to differences in soil water content.

In contrast to urea and N-containing inorganic salts which allow more flexibility with regard to application mode and placement, the highly volatile nature of anhydrous ammonia (AA) restricts its mode of application to subsurface injection which generally results in a highly concentrated band of ammonium. Thus, the effects on NO_2^- oxidizer inhibition and resulting NO_2^- accumulation observed with banded urea applications have been commonly observed with AA (*53*, *55*, *65*). This has not been limited to calcareous soils; for example, following AA application to a slightly acidic loam used for tomato (*Lycopersicon esculentum* L.) production in the Sacramento valley, soil NO_2^- concentrations > 100 μg N g^{-1} soil, and N_2O fluxes > 4 mg m^{-2} h^{-1} were observed (*53*). Increasing depth of AA placement was found to result in increased N_2O emissions in an uncropped clay loam (*72*). In contrast, in an irrigated sand used for corn production, seasonal N_2O emissions following AA applied at a shallower depth (10-12 cm) were approximately twice as much as N_2O emissions following AA applied at the more conventional depth (15-20 cm) (*73*).

N_2O Emissions from Different N Fertilizers in Field Experiments

Field studies in which N_2O emissions resulting from different types of fertilizers were compared in side-by-side experiments are shown in Table I. Data from experiments across several growing seasons and seven locations are included. Nitrous oxide emissions were greater after AA than after U applications at the majority of sites. In some experiments (*65*, *70*, *74*), both fertilizer type and placement were varied among treatments because typical fertility practices were evaluated, and this may have influenced the results. In all the experiments, AA was injected, but U was either subsurface banded, broadcast, disked after broadcasting or applied as liquid followed by roto-tillage. High levels of NH_3 that may occur with U banding are probably reduced when U is broadcast (*74*). At three sites, both AA and U were subsurface banded (i.e. injected). At one of these sites, emissions of N_2O after AA application were twice as high during one growing season in a no-till (NT) corn system in TN, U.S.A. (*69*), but at two other sites in NT and RT (reduced or conservation tillage) wheat systems in South Manitoba, Canada, there were no differences in N_2O emissions among AA, subsurface banded U, and broadcast U treatments. At the S. Manitoba sites, differences in precipitation and soil texture had a greater effect on N_2O fluxes than fertilizer practice. The authors suggested that the presence of a relatively large pool of mineralizable N dampens the effect of N inputs on N_2O emissions in these fertile Chernozem soils.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Table I. Direct N_2O emissions in field experiments with different fertilizers

Ref.	*Fert.*	*kg N ha^{-1}*	*Placement*	*% N_2O*[1]	*Expt. (d)*[2]	*Crop*	*Tillage*	*Soil texture*	*pH*	*Region*
78	AS	125	Surface sprayed	0.18	96	Fallow	Roto			IA, U.S.A.
	U		Surface sprayed	0.14						
	CN		Surface sprayed	0.04						
74	AA	180	Injected	1.29	140	Fallow	Roto	si.l., c.l., scl.	6.9-7.9	IA, U.S.A.
	AqA		Surface sprayed	0.07						
	U		Surface sprayed	0.08						
	CN		Surface sprayed	0.03						
69	AA	168	Injected	7.33	168	Corn	NT	si.l.	6.6	TN, U.S.A.
	U		Injected	3.77						
70	AA	120	Injected	$3.01^{n.c.}$	206	Corn	CT	si.l.	6.0-6.6	MN, U.S.A.
	UAN		Surface sprayed	$0.99^{n.c.}$						
	U		Broadcast	$0.58^{n.c.}$						
	AA	120	Injected	$3.46^{n.c.}$	206	Corn	RT	si.l.	6.0-6.6	MN, U.S.A.
	UAN		Surface sprayed	$1.03^{n.c.}$						
	U		Broadcast	$0.64^{n.c.}$						
	AA	120	Injected	$1.95^{n.c.}$	206	Corn	NT	si.l.	6.0-6.6	MN, U.S.A.
	UAN		Surface sprayed	$1.03^{n.c.}$						

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Ref.	*Fert.*	*kg N ha^{-1}*	*Placement*	*% N_2O*[1]	*Expt. (d)*[2]	*Crop*	*Tillage*	*Soil texture*	*pH*	*Region*
	U		Broadcast	0. 96[n.c.]						
65	AA	146	Injected	1.47[n.c.]	(3)168	Corn	CT	si.l.	6.0-6.6	MN, U.S.A.
	U		Broadcast/disked	0.69[n.c.]						
75	AA	80	Injected	0.53	(3)134-211	Wheat	NT	c.		S. Manitoba, Canada
	U		Injected	0.96						
	U		Broadcast	1.19						
	AA	80	Injected	0.13	(3)118-162	Wheat	CT	c.l.		S. Manitoba, Canada
	U		Injected	0.04						
	U		Broadcast	0.02						
81	U	120	Surface banded	0.30	(2)174	Corn	NT	c.l.	7.6	CO, U.S.A.
	UAN		Surface banded	0.20						
73	U	185	Broadcast/disked	0.19	(2) 180	Corn	CT	l.s.	4.7	MN, U.S.A.
	AA		Injected	0.30						

AS: Ammonium sulfate; AA: Anhydrous ammonia; UAN: Urea ammonium nitrate; U: Urea; CN: Calcium nitrate; CT: Conventional tillage; RT: Reduced tillage; NT: No-till; si.l.: Silt loam; c.: Clay; c.l.: Clay loam; l.s.: loamy sand. [1] Percentage of applied N emitted as N_2O, calculated after subtracting emissions from a non-fertilized control; *n.c.*: no control. [2] Duration of experiments in each year; in parentheses number of growing seasons during which measurements were taken.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Nitrous oxide fluxes are typically attributed to denitrification if high N_2O fluxes coincide with high percent water filled pore space (WFPS) or NO_3^- concentrations (*69*, *75*). In an intensively managed grassland in Scotland, U.K., N_2O was mainly lost by denitrification, and so U proved to be better suited for the prevailing cool and wet conditions than ammonium nitrate (*76*). Thus, climatic conditions are an important consideration when fertilizer choices are made.

Although in earlier studies nitrification was identified as the main source of N_2O after application of U (*16*, *77*, *78*) and AA (*74*, *79*), few investigations have been conducted to validate the process of N_2O production via nitrification, probably because of the methodological difficulties of separating nitrification from denitrification pathways of N_2O production. In a recent study (*65*), nitrification as source of N_2O several weeks after application of AA in a conservation tillage corn system was probably important because the highest seasonal N_2O fluxes occurred when the WFPS was <50% and soil NO_2^- levels were at their seasonal peak. Nitrification was also identified as the main source of N_2O in soils amended with $(NH_4)_2SO_4$ (*16*, *17*, *78*), $NH_4NO_3^-$ (*80*), and UAN (*81*). The role of nitrification in producing N_2O under aerobic conditions has been acknowledged, but there is less certainty about the pathways by which N_2O is generated with different fertilizers under partially anaerobic conditions or over extended time periods.

Greenhouse Gas Emissions Associated with Fertilizer Production

In 2008, worldwide consumption of synthetic fertilizer N was 96.8 million metric tons (Tg) (*82*). Urea is the most common fertilizer used worldwide, with a contribution to total N fertilizer consumption of 57% (*82*) (Table II). Worldwide AA use is not very large compared to the other N forms. In North America in 2007, 40% of all fertilizer N was applied as U, 26% as AA, and 21% as liquid UAN (*7*).

The proportion of a cropping system's net greenhouse gas emissions due to the manufacture and transport of fertilizer varies depending on crop rotation, farming intensity, tillage practice and fertilizer choice. In a conventionally-tilled continuous corn system in NE, U.S.A., 41% of the annual total global warming potential (GWP), including the offset for C sequestration, was estimated to be due to greenhouse gas emissions generated during N fertilizer production and transport (*83*). In contrast, in a no-till corn-soybean-wheat rotation in MI, U.S.A., the GWP of fertilizer manufacture and transport was estimated to be 180% of the system's net GWP (*84*). Since fertilizer production contributes substantially to cropping systems' overall GWP, differences in energy consumption and greenhouse gas emissions during production and transportation of N fertilizer among the different types deserve closer examination.

Estimates of GWP for each N fertilizer product (Table III) vary mainly depending on the manufacturing technology used, so there seems to be considerable potential to lower greenhouse gas emissions of the manufacturing process if the most advanced technology were used in all the fertilizer plants. The higher GWP of NO_3^- containing fertilizers is due to N_2O emitted during nitric acid production. Technology is available to reduce emission of N_2O during nitric acid production by about 70 to 85% (*85*). Post-production emissions (transportation) for N fertilizers have been estimated at 0.04 kg CO_2-C_e kg^{-1} N (*87*). For N and P compound fertilizers (e.g. mono- and di-ammonium phosphate), the sources of the discrepancy among GWP estimates (0.69 to 1.74 CO_2-C_e kg^{-1} N) could not be identified in a review of reports on GWP for fertilizer production (*88*).

Table II. Worldwide fertilizer consumption. Source: IFA, 2008 (*82*)

Fertilizer	*Tg N*	*%*
Urea	55.53	57.2
NPK	8.23	8.5
Other	6.88	7.1
Ammonium phosphate	6.02	6.2
Ammonium nitrate	4.93	5.1
N solutions	4.69	4.8
Ammonia direct	3.45	3.6
Calcium ammonium nitrate	3.01	3.1
Ammonium sulfate	2.76	2.9
Other N phosphates	1.42	1.5
Potassium nitrate	0.07	0.1
TOTAL	96.81	100.0

Table III. Global warming potential (GPW) associated with N fertilizer production

Fertilizer product	*GPW (kg CO_2-C kg^{-1} N)*	*Ref.*
Ammonia	0.53 – 0.77	*7, 85*
Urea	0.69 – 0.93 [1]	*7, 85*
Ammonium nitrate	1.94	*86*
Urea ammonium nitrate (liq.)	1.24 – 1.36 [2]	

[1] No credit included for CO_2 consumption during manufacturing because most of the CO_2 will be emitted to the atmosphere after application of the urea. [2] Calculated based on the above GWP values of ammonium nitrate (50%) and urea (50%) plus a small amount of energy for mixing, cooling and storage (*85*).

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Table IV. Direct N_2O emissions (% of applied N) from controlled release fertilizers in field experiments

Ref.	*Fert.*	*Placement*	*% N_2O*[1]	*Expt. (d)*[2]	*Crop*	*% yield*	*Tillage*	*Texture*	*pH*	*Location*
98	U	Injected in furrows	1.12	(2)97	corn		CT	c.l.	7.2	CO, U.S.A.
	U+np		0.49							
	U+ECC		0.6							
93	AA+AP	Injected, fall	4.75	350	corn	100	RT	l.	6.9	IA, U.S.A.
	AA+AP+np		5.62			110				
	AA+AP	Injected, fall	4.65	350	corn	100	RT	c.l.	7.7	IA, U.S.A.
	AA+AP+np		4.21			103				
97	U	Broadcast, incorp.	0.38	120	wheat	100	NT	l.	8.1	Delhi, India
	U+DCD		0.33			111				
	U+SBT-b		0.33			107				
	U+SBT-f		0.30			109				
	U	Broadcast, incorp.	0.43	120	wheat	100	CT	l.	8.1	Delhi, India
	U+DCD		0.32			108				
	U+SBT-b		0.32			106				
	U+SBT-f		0.29			108				
96	U	Banded (depth 8 cm)	0.37	90	barley[3]	100	CT	c.	7.6	CO, U.S.A.
	U+DCD		0.20			108				
	POCU		0.29			88				

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Ref.	*Fert.*	*Placement*	*% N_2O*[1]	*Expt. (d)*[2]	*Crop*	*% yield*	*Tillage*	*Texture*	*pH*	*Location*
96	U	Banded (depth 5 cm)	2.02	160	corn	100	CT	l.	5.6	Koryama, Japan
	POCU		0.59			112				
99	U+AN	Banded&broadcast	0.5	(2)130	potato[4]	100	CT	l.s.	4.9-6.7	MN, U.S.A.
	POCU	Broadcast, disked	0.3			100				
95	U	Broadcast, split appl.	0.67	(2)78	corn	100		si.l.	6.7	Nanjing, China
	UF	Broadcast, single appl.	0.5			126				
	U+DCD+HQ	Broadcast, single appl.	0.25			119				
	U-Ca-Mg-P	Broadcast, single appl.	1.06			90				
	POCU	Broadcast, single appl.	1.05			98				
	SCU	Broadcast, single appl.	0.88			130				
81	U	Banded, surface	0.32	(2)174	corn	100	NT	c.l.	7.6	CO, U.S.A.
	POCU		0.20			96				
	U-UI-DCD[5]		0.09			93				
	UAN	Banded, surface	0.18			100	NT	c.l.	7.6	CO, U.S.A.
	UAN+UI+DCD[5]		0.09			106				

Continued on next page.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Table IV. (Continued). Direct N_2O emissions (% of applied N) from controlled release fertilizers in field experiments

Ref.	*Fert.*	*Placement*	*% N_2O^1*	*Expt. (d)^2*	*Crop*	*% yield*	*Tillage*	*Texture*	*pH*	*Location*
94	U	Broadcast, sidedress	0.20	(3)180	corn	100	CT	si.l.	5.8	MN, U.S.A.
	POCU		0.36			94				
	U-UI-DCD^5		0.19			95				
	U	Broadcast, sidedress	0.31		corn	100	NT	si.l.	6.0	MN, U.S.A.
	POCU		0.27			96				
	U-UI-DCD^5		0.14			95				

U: Urea; np: Nytrapyrin; AA: Anhydrous ammonia; AP: Diammonium phosphate; DCD: Dicyandiamide; SBT-b: S-benzylisothiouronium- butanoate; SBT-f: SBT-fuorate; POCU: Polymer-coated urea; AN: Ammonium nitrate; UF: urea formaldehyde; HQ: Hydroquinone (urease inhibitor); U-Ca-Mg-P: Calcium-magnesium-phosphate-coated urea; SCU: Sulfur-coated urea; c.: Clay; l.: Loam; si.: Silt; s.: sand [1] Percentage of applied N fertilizer emitted as N_2O during the experiment without subtraction of an unfertilized control; [2] Duration of experiments in each year and in parentheses number of years during which measurements were taken; [3] *Hordeum vulgare* L.; [4] *Solanum tuberosum* L.; [5] Composite of urea, and urease and nitrification inhbitors.

Taking a life cycle analysis approach in accounting for differences in greenhouse gas emissions among cropping systems can provide accurate assessments of management practices with respect to their climate benefit. Seasonal N_2O emissions in a continuous corn rotation in MN, U.S.A., amounted to 275 and 128 kg CO_2-C_e ha^{-1} with AA and U fertilization, respectively (*65*), but accounting for emissions during N fertilizer production using the coefficients at the low end of the range of values shown in Table III would raise the emissions to 352 and 228 kg CO_2-C_e ha^{-1} with AA and U fertilization. Thus, in the overall analysis, greenhouse gas emissions from the U-fertilized system were 64% of those of the AA-fertilized system, rather than 47% when solely soil N_2O emissions between the two systems are compared. In another study in a no-till continuous corn system in CO, U.S.A., 2008 growing season N_2O emissions were significantly greater in U- (84 kg CO_2-C_e ha^{-1}) than in UAN-fertilized plots (45 kg CO_2-C_e ha^{-1}) (*81*), but inclusion of greenhouse gas emissions generated during the production of these fertilizers would bring the total emissions to 222-270 for U- and to 295-319 kg CO_2-C_e ha^{-1} for UAN-fertilized plots. In this study, overall greenhouse gas emissions associated with fertilization, including both soil N_2O and upstream energy consumption for fertilizer production, in the UAN were not different or higher than in the U treatment, even though soil N_2O emissions showed the opposite effect.

Controlled Release Fertilizers

Controlled- or slow-release fertilizers and inhibitors, sometimes referred to as enhanced efficiency fertilizers, have the potential to increase crop N recovery and yields and to reduce NO_3^- leaching and gaseous N losses. Slow and controlled-release fertilizers (CRFs) have been classified into (chemically altered) organic N low-solubility compounds, such as urea-formaldehyde or isobutyledene-diurea, and fertilizers in which a physical barrier controls the release of plant available N, such as polymer-, sulfur-, and calcium magnesium phosphate-coated fertilizers (*89*). Nitrification inhibitors, such as nitrapyrin and dicyandiamide (DCD) depress nitrifier activity over a certain period of time. Urease inhibitors slow down the rate of U hydrolysis in the soil. Stabilized fertilizers are those amended with a nitrification inhibitor during production.

In the last two decades, applying CRFs in field crop systems has received much interest. According to a recent meta-analysis (*90*), using field experiment data (113 data sets from 35 studies), nitrification inhibitors significantly reduced N_2O emissions by 38% (95% confidence interval -44% to -31%), but urease inhibitors were not effective in lowering N_2O emissions. Polymer-coated fertilizers (PCFs) gave mixed results, being very effective in reducing N_2O emissions in imperfectly drained grasslands of a particular region (Scotland, U.K.), but ineffective in well-drained upland soils in Japan. Most of the studies considered in this meta-analysis measured N_2O emissions during the cropping season although application of CRFs may affect emissions beyond this period. Some studies have reported that excessively slow delay in the release of N from certain PCFs may result in high residual soil or soil-water N levels following

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

harvest and/or into the following spring which could contribute to subsequent N_2O emissions (*91*, *92*). Thus, ideally, PCF formulations need to be selected so that their release rates and application rates are matched to a particular cropping system.

The results of some recent studies, in which different types of CRFs were compared, are summarized in Table IV. The efficacy of some nitrification inhibitors with current formulations may be limited to only one growing season. For example, in a silty clay loam with a corn/soybean rotation in the Midwest, U.S., N_2O emissions after fall-applied AA with nitrapyrin amendment were reduced in late fall and early spring following AA with nitrapyrin application, but the cumulative annual emissions did not differ from those measured in control plots without nitrapyrin (*93*). A recent three-year study in rainfed corn in the Midwest, U.S., showed no reduction in N_2O emissions using either a polymer-coated urea or urea impregnated with the nitrification inhibitor DCD and a urease inhibitor compared with conventional urea when all three products were applied several weeks after planting (*94*). On the other hand, DCD and hydroquinone reduced N_2O emissions by 33-63% during each of two maize growing seasons in a rainfed system in the subtropical region of Nanjing, China (*95*). Nitrous oxide emissions were also significantly lowered after U fertilization combined with the nitrification inhibitor DCD in a sandy loam soil in a barley (*Hordeum vulgare* L.) system in CO, U.S.A. (*96*). In another study with intensive grassland in Scotland, U.K. (*76*), only a nitrification inhibitor reduced N_2O emissions compared to U alone, whereas urease inhibitors, combinations of both nitrification and urease inhibitors, as well as a controlled-release, coated U fertilizer were all ineffective in lowering soil NO_3^- concentrations and N_2O emissions.

Two relatively new nitrification inhibitors, S-benzylisothiouronium butanoate (SBT-butanoate), S-benzylisothiouronium furoate (SBT-furoate), were compared to DCD in an irrigated wheat system with two tillage practices in the subtropical, semi-arid Delhi region in India (*97*). All nitrification inhibitors reduced N_2O emissions to a similar extent compared to U alone under both conventional tillage and no-till (*97*). Among the various types of nitrification inhibitors, encapsulated calcium carbide (ECC) has also been tested with some success. This material was subsurface banded with U and significantly reduced N_2O emissions (*98*). Some caution is advised with this method. Since both nitrification and reduction of N_2O are inhibited by ECC, there is the potential of enhanced N_2O flux due to denitrification from residual NO_3^-.

The release of plant-available N from coated fertilizers is temperature and moisture dependent. In irrigated barley grown in a sandy-loam soil in CO, U.S.A., polyolefin-coated U decreased N_2O emissions by 71% compared to U during 21 d after fertilization, but after this period N_2O emissions were greater from the polymer-coated fertilizer than urea fertilizer during the remainder of the growing season (*100*). High N_2O emission was attributed to continued release of N from this CRF (*100*). The use of the same type of CRF reduced N_2O emissions during a corn growing season (120 d) in another experiment under different climatic conditions in Koryama, Japan (*96*), by two thirds while corn plant recovery of N was twice as high as with U fertilization. In contrast, three encapsulated fertilizers,

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Ca-Mg-P-, polymer- and sulfur-coated U, enhanced N_2O emissions by up to 100% compared to regular U in the subtropical climate in Nanjing, China (*95*). High soil temperatures (22 - 31°C) during the growing season may have influenced the release of N from these CRFs, and in addition, N_2O emissions were increased by precipitation shortly after fertilization.

Summary

Among synthetic N fertilizer sources, AA likely causes the greatest N_2O emissions because it forms zones of high NH_3 concentration that raise the soil pH and lead to accumulation of NO_2^-, which is probably the main substrate of N_2O production during nitrification. To date, we count 6 separate studies conducted on 8 different soil types comparing AA to urea in side-by-side trials (*65*, *69*, *70*, *73–75*). Of these, only one study conducted in two Canadian wheat production systems (*75*) showed no effect of fertilizer source. The lower rate of N application (80 kg N ha^{-1}) used in this study compared with the other 5 studies (≥ 120 kg N ha^{-1}) suggests that the mechanism(s) responsible for higher N_2O emissions with AA depend in the rate of N addition, but more study is needed to evaluate this hypothesis. Other alkaline-forming fertilizers, such as U, also tend to produce more N_2O when they are locally concentrated, e.g. in bands, rather than dispersed evenly in the soil. The advantages of banding N fertilizer in terms of crop N recovery and yields must be evaluated against the drawback of potentially higher N_2O emissions in varied cropping systems. Among the controlled release fertilizers, nitrification inhibitors lower N_2O emissions, at least within the time frame of one growing season, whereas urease inhibitors are generally ineffective. The CRFs, which control the release of plant available N by a physical barrier, need to be evaluated further because their efficacy has varied widely in different environments and climatic conditions. The greenhouse gas emissions generated during the production of synthetic fertilizers depend on the technology of the industrial process and differ substantially among the various types of fertilizers. Adding the manufacturing and field emissions can shift the overall greenhouse gas emissions among fertility practices depending on the fertilizer type being used. Better knowledge about the pathways of N_2O production from different fertilizers under varying soil and water conditions will enable fertilizer users to choose appropriate N sources and placement methods.

Acknowledgments

We thank M.A.A. Adviento-Borbe, W.R. Horwath, and the anonymous reviewers for their comments on earlier versions of this chapter.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

References

1. Crutzen, P. J.; Mosier, A. R.; Smith, K. A.; Winiwarter, W. N_2O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmos. Chem. Phys.* **2008**, *8* (2), 389–395.
2. Mosier, A.; Kroeze, C.; Nevison, C.; Oenema, O.; Seitzinger, S.; Van Cleemput, O. Closing the global N_2O budget: Nitrous oxide emissions through the agricultural nitrogen cycle: OEDC/IPCC/IEA phase II development of IPCC guideline for national greenhouse gas methodology. *Nutr. Cycling Agroecosyst.* **1998**, *52* (2-3), 225–248.
3. Davidson, E. A. The contribution of manure and fertilizer nitrogen to atmospheric nitrous oxide since 1860. *Nature Geosci.* **2009**, *2* (9), 659–662.
4. Eichner, M. J. Nitrous oxide emissions from fertilized soils: Summary of available data. *J. Environ. Qual.* **1990**, *19* (2), 272–280.
5. Bouwman, A. F. Direct emission of nitrous oxide from agricultural soils. *Nutr. Cycling Agroecosyst.* **1996**, *46* (1), 53–70.
6. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. Emissions of N_2O and NO from fertilized fields: Summary of available measurement data. *Global Biogeochem. Cycles* **2002**, *16* (4).
7. Snyder, C. S.; Bruulsema, T. W.; Jensen, T. L.; Fixen, P. E. Review of greenhouse gas emissions from crop production systems and fertilizer management effects. *Agric. Ecosyst. Environ.* **2009**, *133* (3-4), 247–266.
8. Stehfest, E.; Bouwman, L. N_2O and NO emission from agricultural fields and soils under natural vegetation: summarizing available measurement data and modeling of global annual emissions. *Nutr. Cycling Agroecosyst.* **2006**, *74* (3), 207–228.
9. Galloway, J. N.; Dentener, F. J.; Capone, D. G.; Boyer, E. W.; Howarth, R. W.; Seitzinger, S. P.; Asner, G. P.; Cleveland, C. C.; Green, P. A.; Holland, E. A.; Karl, D. M.; Michaels, A. F.; Porter, J. H.; Townsend, A. R.; Vorosmarty, C. J. Nitrogen cycles: past, present, and future. *Biogeochemistry* **2004**, *70* (2), 153–226.
10. Burger, M.; Matiasek, M. New Approaches to Distinguish between Nitrification and Denitrification as Sources of Nitrous Oxide. In *Nitrous Oxide Emissions Research Progress*; Sheldon, A. I., Barnhart, E. P., Eds.; Nova Publishers: New York, 2009; pp 167−178.
11. Firestone, M. K.; Davidson, E. A. Microbiological Basis of NO and N_2O Production and Consumption. In *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*; Andreae, M. O., Schimel, D. S., Eds.; Wiley: New York, 1989; pp 7−21.
12. Tiedje, J. M. Ecology of denitrification and dissimilatory nitrate reduction to ammonium. In *Biology of Anaerobic Microorganisms*; Zehnder, A. J. B., Ed.; John Wiley: New York, 1988; pp 179−244.
13. Wrage, N.; Velthof, G. L.; van Beusichem, M. L.; Oenema, O. Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biol. Biochem.* **2001**, *33* (12-13), 1723–1732.
14. Shapleigh, J. P. The denitrifying prokaryotes. *Prokaryotes* **2006**, *2*, 769–792.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

15. Shoun, H.; Kim, D. H.; Uchiyama, H.; Sugiyama, J. Denitrification by fungi. *FEMS Microbiol. Lett.* **1992**, *94* (3), 277–281.
16. Bremner, J. M.; Blackmer, A. M. Nitrous oxide emission from soils during nitrification of fertilizer nitrogen. *Science (Washington DC)* **1978**, *199* (4326), 295–296.
17. Bremner, J. M.; Blackmer, A. M. Effects of acetylene and soil water content on emission of nitrous oxide from soils. *Nature (London)* **1979**, *280*, 380–381.
18. Hooper, A. B.; Terry, K. R. Hydroxylamine oxidoreductase of *Nitrosomonas* production of nitric oxide from hydroxylamine. *Biochim. Biophys. Acta* **1979**, *571* (1), 12–20.
19. Bremner, J. M.; Blackmer, A. M.; Waring, S. A. Formation of nitrous-oxide and dinitrogen by chemical decomposition of hydroxylamine in soils. *Soil Biol. Biochem.* **1980**, *12* (3), 263–269.
20. Tenuta, M.; Beauchamp, E. G. Nitrous oxide production from urea granules of different sizes. *J. Environ. Qual.* **2000**, *29* (5), 1408–1413.
21. Subbarao, G. V.; Ito, O.; Sahrawat, K. L.; Berry, W. L.; Nakahara, K.; Ishikawa, T.; Watanabe, T.; Suenaga, K.; Rondon, M.; Rao, I. M. Scope and strategies for regulation of nitrification in agricultural systems-challenges and opportunities. *Crit. Rev. Plant Sci.* **2006**, *25* (4), 303–335.
22. Arp, D. J.; Stein, L. Y. Metabolism of inorganic N compounds by ammonia-oxidizing bacteria. *Crit. Rev. Biochem. Mol. Biol.* **2003**, *38* (6), 471–495.
23. Minami, K.; Fukushi, S. Emission of nitrous oxide from a well-aerated Andosol treated with nitrite and hydroxylamine. *Soil Sci. Plant Nutr.* **1986**, *32* (2), 233–237.
24. Ritchie, G. A. F.; Nicholas, D. J. Identification of the sources of nitrous oxide produced by oxidative and reductive processes in *Nitrosomonas europaea. Biochem. J.* **1972**, *126* (5), 1181.
25. Poth, M.; Focht, D. D. Nitrogen-15 kinetic analysis of nitrous oxide production by Nitrosomonas europaea: An examination of nitrifier denitrification. *Appl. Environ. Microbiol.* **1985**, *49* (5), 1134–1141.
26. Goreau, T. J.; Kaplan, W. A.; Wofsy, S. C.; McElroy, M. B.; Valois, F. W.; Watson, S. W. Production of NO_2^- and N_2O by nitrifying bacteria at reduced concentrations of oxygen. *Appl. Environ. Microbiol.* **1980**, *40* (3), 526–532.
27. Castignetti, D.; Yanong, R.; Gramzinski, R. Heterotrophic nitrification among denitrifiers. *Appl. Environ. Microbiol.* **1984**, *47*, 620–623.
28. Davidson, E. A.; Swank, W. T.; Perry, T. O. Distinguishing between nitrification and denitrification as sources of gaseous nitrogen production in soil. *Appl. Environ. Microbiol.* **1986**, *52* (6), 1280–1286.
29. Venterea, R. T. Nitrite-driven nitrous oxide production under aerobic soil conditions: kinetics and biochemical controls. *Global Change Biol.* **2007**, *13* (8), 1798–1809.
30. Kool, D. M.; Wrage, N.; Zechmeister-Boltenstern, S.; Pfeffer, M.; Brus, D.; Oenema, O.; Van Groenigen, J. W. Nitrifier denitrification can be a source of N_2O from soil: a revised approach to the dual-isotope labelling method. *Eur. J. Soil Sci.* **2010**, *61* (5), 759–772.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

31. Verstraete, W.; Philips, S. Nitrification-denitrification processes and technologies in new contexts. *Environ. Pollut.* **1998**, *102*, 717–726.

32. Webster, E. A.; Hopkins, D. W. Contributions from different microbial processes to N_2O emission from soil under different moisture regimes. *Biol. Fert. Soils* **1996**, *22* (4), 331–335.

33. Kool, D. M.; Wrage, N.; Oenema, O.; Dolfing, J.; Van Groenigen, J. W. Oxygen exchange between (de) nitrification intermediates and H2O and its implications for source determination of NO_3^- and N_2O: a review. *Rapid Commun. Mass Spectrom.* **2007**, *21* (22), 3569–3578.

34. Wrage, N.; van Groenigen, J. W.; Oenema, O.; Baggs, E. M. A novel dual-isotope labelling method for distinguishing between soil sources of N_2O. *Rapid Commun. Mass Spectrom.* **2005**, *19* (22), 3298–3306.

35. VanCleemput, O.; Samater, A. H. Nitrite in soils: Accumulation and role in the formation of gaseous N compounds. *Fert. Res.* **1996**, *45* (1), 81–89.

36. Bremner, J. M. Sources of nitrous oxide in soils. *Nutr. Cycling Agroecosyst.* **1997**, *49* (1-3), 7–16.

37. Venterea, R. T.; Rolston, D. E. Mechanisms and kinetics of nitric and nitrous oxide production during nitrification in agricultural soil. *Global Change Biol.* **2000**, *6* (3), 303–316.

38. Stevenson, F. J.; Harrison, R. M.; Wetselaar, R.; Leeper, R. A., Nitrosation of soil organic matter. Nature of gases produced by reaction of nitrite with lignins, humic substances, and phenolic constituents under neutral and slightly acidic conditions. *Soil Sci. Soc. Am. Proc.* **1970**, *34* (3), 430.

39. Thorn, K. A.; Mikita, M. A. Nitrite fixation by humic substances: Nitrogen-15 nuclear magnetic resonance evidence for potential intermediates in chemodenitrification. *Soil Sci. Soc. Am. J.* **2000**, *64* (2), 568–582.

40. Stevenson, F. J.; Swaby, R. J. Nitrosation of soil organic matter: I. Nature of gases evolved during nitrous acid treatment of lignins and humic substances. *Soil Sci. Soc. Am. Proc.* **1964**, *28*, 773–778.

41. Sutka, R. L.; Ostrom, N. E.; Ostrom, P. H.; Breznak, J. A.; Gandhi, H.; Pitt, A. J.; Li, F. Distinguishing nitrous oxide production from nitrification and denitrification on the basis of isotopomer abundances. *Appl. Environ. Microbiol.* **2006**, *72* (1), 638–644.

42. Jinuntuya-Nortman, M.; Sutka, R. L.; Ostrom, P. H.; Gandhi, H.; Ostrom, N. E. Isotopologue fractionation during microbial reduction of N_2O within soil mesocosms as a function of water-filled pore space. *Soil Biol. Biochem.* **2008**, *40* (9), 2273–2280.

43. Bouman, O. T.; Curtin, D.; Campbell, C. A.; Biederbeck, V. O.; Ukrainetz, H. Soil acidification from long term use of anhydrous ammonia and urea. *Soil Sci. Soc. Am. J.* **1995**, *59* (5), 1488–1494.

44. Mulvaney, R. L.; Khan, S. A.; Mulvaney, C. S. Nitrogen fertilizers promote denitrification. *Biol. Fertil. Soils* **1997**, *24* (2), 211–220.

45. Hauck, R. D.; Stephens, H. F. Nitrification of nitrogen fertilizers - effect of nitrogen source size and pH of granule and concentration. *J. Agric. Food. Chem.* **1965**, *13* (6), 486.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

46. Blackmer, A. M.; Bremner, J. M. Inhibitory effect of nitrate on nitrous oxide to molecular nitrogen by soil microorganisms. *Soil Biol. Biochem.* **1978**, *10*, 187–191.
47. Firestone, M. K.; Firestone, R. B.; Tiedje, J. M. Nitrous oxide from soil denitrification: Factors controlling its biological production. *Science (Washington DC)* **1980**, *208*, 749–751.
48. Nägele, W.; Conrad, R. Influence of pH on the release of NO and N_2O from fertilized and unfertilized soil. *Biol. Fertil. Soils* **1990**, *10* (2), 139–144.
49. Betlach, M. R.; Tiedje, J. M. Kinetic explanation for accumulation of nitrite, nitric oxide, and nitrous oxide during bacterial denitrification. *Appl. Environ. Microbiol.* **1981**, *42* (6), 1074–1084.
50. Rachhpalsingh; Nye, P. H. The effect of soil pH and high urea concentrations on urease activity in soil. *J. Soil. Sci.* **1984**, *35* (4), 519–527.
51. Cabrera, M. L.; Kissel, D. E.; Bock, B. R. Urea hydrolysis in soil: Effects of urea concentration and soil pH. *Soil Biol. Biochem.* **1991**, *23* (12), 1121–1124.
52. Mikkelsen, R., The four fertilizer rights: Selecting the right source. *Crops Soil* **2009**, *May-June*, 28−31.
53. Venterea, R. T.; Rolston, D. E. Nitric and nitrous oxide emissions following fertilizer application to agricultural soil: Biotic and abiotic mechanisms and kinetics. *J. Geophys. Res. Atmos.* **2000**, *105* (D12), 15117–15129.
54. Minami, K.; Fukushi, S. Effects of phosphate and calcium carbonate application on emission of N_2O from soils under aerobic conditions. *Soil Sci. Plant Nutr.* **1983**, *29* (4), 517–524.
55. Chalk, P. M.; Keeney, D. R.; Walsh, L. M. Crop recovery and nitrification of fall and spring applied anhydrous ammonia. *Agron. J.* **1975**, *67* (1), 33–37.
56. Chapman, H. D.; Liebig, G. F. Field and laboratory studies of nitrite accumulation in soils. *Soil Sci. Soc. Am. Proc.* **1952**, *16* (3), 276–282.
57. Engel, R.; Liang, D. L.; Wallander, R.; Bembenek, A. Influence of Urea Fertilizer Placement on Nitrous Oxide Production from a Silt Loam Soil. *J. Environ. Qual.* **2010**, *39* (1), 115–125.
58. Firestone, M. K.; Smith, M. S.; Firestone, R. B.; Tiedje, J. M. Influence of nitrate, nitrite, and oxygen on the composition of the gaseous products of denitrification in soil. *Soil Sci. Soc. Am. J.* **1979**, *43* (6), 1140–1144.
59. Gaskell, J. F.; Blackmer, A. M.; Bremner, J. M. Comparison of effects of nitrate, nitrite, and nitric-oxide on reduction of nitrous-oxide to dinitrogen by soil microorganisms. *Soil Sci. Soc. Am. J.* **1981**, *45* (6), 1124–1127.
60. Anthonisen, A. C.; Loehr, R. C.; Prakasam, T. B. S.; Srinath, E. G. Inhibition of nitrification by ammonia and nitrous acid. *J. − Water Pollut. Control Fed.* **1976**, *48* (5), 835–852.
61. Yadvindersingh; Malhi, S. S.; Nyborg, M.; Beauchamp, E. G. Large granules, nests or bands - methods of increasing efficiency of fall-applied urea for small grains in North America. *Fertil. Res.* **1994**, *38* (1), 61–87.
62. Hawkins, S.; Robinson, K.; Layton, A.; Sayler, G. Limited impact of free ammonia on Nitrobacter spp. inhibition assessed by chemical and molecular techniques. *Bioresour. Technol.* **2010**, *101* (12), 4513–4519.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

63. Norman, R. J.; Kurtz, L. T.; Stevenson, F. J. Solubilization of soil organic matter by liquid anhydrous ammonia. *Soil Sci. Soc. Am. J.* **1987**, *51* (3), 809–812.
64. Burford, J. R.; Bremner, J. M. Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposible soil organic matter. *Soil Biol. Biochem.* **1975**, *7*, 389–394.
65. Venterea, R. T.; Dolan, M. S.; Ochsner, T. E. Urea Decreases Nitrous Oxide Emissions Compared with Anhydrous Ammonia in a Minnesota Corn Cropping System. *Soil Sci. Soc. Am. J.* **2010**, *74* (2), 407–418.
66. Khalil, M. I.; Schmidhalter, U.; Gutser, R. N_2O, NH_3 and NOx emissions as a function of urea granule size and soil type under aerobic conditions. *Water, Air, Soil Pollut.* **2006**, *175* (1-4), 127–148.
67. Smith, C. J.; Brandon, M.; Patrick, W. H. Nitrous oxide emission following urea N fertilization of wetland rice. *Soil Sci. Plant Nutr.* **1982**, *28* (2), 161–171.
68. Cheng, W.; Nakajima, Y.; Sudo, S.; Akiyama, H.; Tsuruta, H. N2O and NO emissions from a field of Chinese cabbage as influenced by band application of urea or controlled-release urea fertilizers. *Nutr. Cycling Agroecosyst.* **2002**, *63* (2-3), 231–238.
69. Thornton, F. C.; Bock, B. R.; Tyler, D. D. Soil emissions of nitric oxide and nitrous oxide from injected anhydrous ammonium and urea. *J. Environ. Qual.* **1996**, *25* (6), 1378–1384.
70. Venterea, R. T.; Burger, M.; Spokas, K. A. Nitrogen oxide and methane emissions under varying tillage and fertilizer management. *J. Environ. Qual.* **2005**, *34* (5), 1467–1477.
71. Drury, C. F.; Reynolds, W. D.; Tan, C. S.; Welacky, T. W.; Calder, W.; McLaughlin, N. B. Emissions of nitrous oxide and carbon dioxide: influence of tillage type and nitrogen placement depth. *Soil Sci. Soc. Am. J.* **2006**, *70* (2), 570–581.
72. Breitenbeck, G. A.; Bremner, J. M. Effects of rate and depth of fertilizer application on emission of nitrous-oxide from soil fertilized with anhydrous ammonia. *Biol. Fert. Soils* **1986**, *2* (4), 201–204.
73. Fujinuma, R.; Venterea, R. T.; Rosen, C. J. *USDA-ARS and University of Minnesota, St. Paul, MN*, unpublished.
74. Breitenbeck, G. A.; Bremner, J. M. Effects of various nitrogen fertilizers on emission of nitrous-oxide from soils. *Biol. Fertil. Soils* **1986**, *2* (4), 195–199.
75. Burton, D. L.; Li, X. H.; Grant, C. A. Influence of fertilizer nitrogen source and management practice on N_2O emissions from two Black Chernozemic soils. *Can. J. Soil. Sci.* **2008**, *88* (2), 219–227.
76. Dobbie, K. E.; Smith, K. A. Impact of different forms of N fertilizer on N_2O emissions from intensive grassland. *Nutr. Cycling Agroecosyst.* **2003**, *67* (1), 37–46.
77. Akiyama, H.; McTaggart, I. P.; Ball, B. C.; Scott, A. N_2O, NO, and NH_3 emissions from soil after the application of organic fertilizers, urea and water. *Water, Air, Soil Pollut.* **2004**, *156* (1-4), 113–129.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

78. Breitenbeck, G. A.; Blackmer, A. M.; Bremner, J. M. Effects of different nitrogen fertilizers on emission of nitrous-oxide from soil. *Geophys. Res. Lett.* **1980**, *7* (1), 85–88.
79. Bremner, J. M.; Breitenbeck, G. A.; Blackmer, A. M. Effect of anhydrous ammonia fertilization on emission of nitrous-oxide from soils. *J. Environ. Qual.* **1981**, *10* (1), 77–80.
80. Hutchinson, G. L.; Guenzi, W. D.; Livingston, G. P. Soil water controls on aerobic soil emission of gaseous nitrogen oxides. *Soil Biol. Biochem.* **1993**, *25* (1), 1–9.
81. Halvorson, A. D.; Del Grosso, S. J.; Alluvione, F. Nitrogen source effects on nitrous oxide emissions from irrigated no-till corn. *J. Environ. Qual.* **2010**, *39* (5), 1554–1562.
82. IFA International Fertilizer Industry Association Database. http://www.fertilizer.org/ifa/Home-Page/STATISTICS (verified 29 May 2011).
83. Adviento-Borbe, M. A. A.; Haddix, M. L.; Binder, D. L.; Walters, D. T.; Dobermann, A. Soil greenhouse gas fluxes and global warming potential in four high-yielding maize systems. *Global Change Biol.* **2007**, *13* (9), 1972–1988.
84. Robertson, G. P.; Paul, E. A.; Harwood, R. R. Greenhouse gases in intensive agriculture: Contributions of individual gases to the radiative forcing of the atmosphere. *Science (Washington DC)* **2000**, *289* (5486), 1922–1925.
85. Kongshaug, G. Energy consumption and greenhouse gas emissions in fertilizer production. In *International Fertilizer Industry Association Technical Conference*, Marrakech, Morocco, 1998.
86. Kramer, K. J.; Moll, H. C.; Nonhebel, S. Total greenhouse gas emissions related to the Dutch crop production system. *Agric., Ecosyst. Environ.* **1999**, *72* (1), 9–16.
87. West, T. O.; Marland, G. A synthesis of carbon sequestration, carbon emissions, and net carbon flux in agriculture: comparing tillage practices in the United States. *Agric., Ecosyst. Environ.* **2002**, *91* (1-3), 217–232.
88. Wood, S.; Cowie, A. A review of greenhouse gas emission factors for fertilizer production. http://www.ieabioenergy-task38.org/publications/ (verified 29 May 2011).
89. Shaviv, A. Advances in controlled-release fertilizers. *Adv. Agron.* **2001**, *71*, 1−49.
90. Akiyama, H.; Yan, X. Y.; Yagi, K. Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N_2O and NO emissions from agricultural soils: meta-analysis. *Global Change Biol.* **2010**, *16* (6), 1837–1846.
91. Zvomuya, F.; Rosen, C. J.; Russelle, M. P.; Gupta, S. C. Nitrate leaching and nitrogen recovery following application of polyolefin-coated urea to potato. *J. Environ. Qual.* **2003**, *32* (2), 480–489.
92. Venterea, R. T.; Hyatt, C. R.; Rosen, C. J., Fertilizer management effects on nitrate leaching and indirect nitrous oxide emissions in irrigated potato production. *J. Environ. Qual.* 2011, In press.

93. Parkin, T. B.; Hatfield, J. L. Influence of nitrapyrin on N_2O losses from soil receiving fall-applied anhydrous ammonia. *Agric. Ecosyst. Environ.* **2010**, *136* (1-2), 81–86.
94. Venterea, R. T.; Maharjan, B.; Dolan, M. S., Fertilizer source and tillage effects on yield-scaled N_2O emissions in a corn cropping system. *J. Environ. Qual.* 2011, In press.
95. Jiang, J. Y.; Hu, Z. H.; Sun, W. J.; Huang, Y. Nitrous oxide emissions from Chinese cropland fertilized with a range of slow-release nitrogen compounds. *Agric. Ecosyst. Environ.* **2010**, *135* (3), 216–225.
96. Shoji, S.; Delgado, J.; Mosier, A.; Miura, Y. Use of controlled release fertilizers and nitrification inhibitors to increase nitrogen use efficiency and to conserve air and water quality. *Commun. Soil Sci. Plant Anal.* **2001**, *32* (7-8), 1051–1070.
97. Bhatia, A.; Sasmal, S.; Jain, N.; Pathak, H.; Kumar, R.; Singh, A. Mitigating nitrous oxide emission from soil under conventional and no-tillage in wheat using nitrification inhibitors. *Agric. Ecosyst. Environ.* **2010**, *136* (3-4), 247–253.
98. Bronson, K. F.; Mosier, A. R.; Bishnoi, S. R. Nitrous oxide emissions in irrigated corn as affected by nitrification inhibitors. *Soil Sci. Soc. Am. J.* **1992**, *56* (1), 161–165.
99. Hyatt, C. R.; Venterea, R. T.; Rosen, C. J.; McNearny, M.; Wilson, M. L.; Dolan, M. S. Polymer-coated urea maintains potato yields and reduces nitrous oxide emissions in a Minnesota loamy sand. *Soil Sci. Soc. Am. J.* **2010**, *74* (2), 419–428.
100. Delgado, J. A.; Mosier, A. R. Mitigation alternatives to decrease nitrous oxides emissions and urea-nitrogen loss and their effect on methane flux. *J. Environ. Qual.* **1996**, *25* (5), 1105–1111.

Downloaded by OHIO STATE UNIV LIBRARIES on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch011

Chapter 12

Discerning Agricultural Management Effects on Nitrous Oxide Emissions from Conventional and Alternative Cropping Systems: A California Case Study

E. C. Suddick,*,[1] K. Steenwerth,[2] G. M. Garland,[1] D. R. Smart,[3] and J. Six[1]

**[1]Department of Plant Sciences, University of California,
Davis, CA, 95616
[2]USDA/ARS, Crops Pathology and Genetics Research Unit,
Davis, CA 95616
[3]Department of Viticulture and Enology, University of California,
Davis, CA, 95616
*E-mail: ecsuddick@ucdavis.edu**

Several decades of research have provided crucial understanding of the production of nitrous oxide (N_2O) from agricultural soils and the major environmental and managerial factors that play a role in the generation of this potent greenhouse gas (GHG). Due to the increase in demand for food production and the concomitant increase in use of N fertilizers to meet this demand, it is more than ever important to quantify the effects of the different factors contributing to N_2O emissions and produce detailed, accurate and reliable annual N_2O emission budgets for current and alternative agricultural systems. Within the diverse cropping systems of California, annual budgets are missing or incomplete for some of the state's more important, high acreage cash crops such as grape and nut crops. Recent research, documented within this paper, highlights the difference in N_2O emissions between conventional and alternative management practices in perennial and annual cropping systems of California. We observed measureable differences in N_2O emissions between standard and conservation irrigation techniques used in a Northern

California almond orchard. Sub-surface drip irrigation had lowered emissions of N_2O (0.006± 0.001 kg N_2O-N ha^{-1}) compared to surface drip (0.08 ± 0.021 kg N_2O-N ha^{-1}) following a four-day fertigation event. In a Northern California vineyard, although not statistically different, standard tillage (ST) led to less N_2O emissions compared to no tillage (NT)/conservation tillage (CT) practices, where cumulative emissions were 0.13 ± 0.021 kg N_2O-N ha^{-1} $season^{-1}$ in the ST system as compared to 0.19 ± 0.017 kg N_2O-N ha^{-1} $season^{-1}$ from the NT system. We also show that the use of pyrolyzed agricultural wastes (biochar) as a soil amendment has the ability to reduce N_2O emissions associated with fertigation peaks by approximately 41%, however, overall cumulative emissions were not statistically different between the biochar amended soils and control soils. Finally, we recommend based on our studies that future investigations in California should include longer term and more robust sampling to be able to create more accurate future emission budgets and mitigate GHG emissions from both vegetable and perennial crops.

Introduction

During the last century, the impact of anthropogenic activities upon the global nitrogen (N) cycle have led to increased emissions of reactive forms of N to the atmosphere, which has affected climate systems through production of air pollutants, including nitrous oxide (N_2O) (*1*). The increase of N_2O in the atmosphere is currently of increasing concern due to its high radiative forcing potential, at approximately 300 times greater than carbon dioxide (CO_2), and its role in stratospheric ozone depletion (*2*, *3*). Soils are the principal source of N_2O, with agricultural soils representing the single largest source of anthropogenic N_2O production (*1*, *4*). Nitrous oxide accounts for approximately 6% of total anthropogenic greenhouse gas (GHG) emissions (*5*). According to the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report:Climate Change 2007, direct and indirect emissions of N_2O from agricultural ecosystems to the atmosphere contribute approximately 6 Tg N yr^{-1}. However, it has been suggested that emissions can be reduced by approximately 0.5 Tg N_2O-N yr^{-1} through improved fertilizer management and alternative irrigation and crop management techniques (*6*).

Nitrous oxide is primarily produced from the microbial processes of denitrification and nitrification and is affected by many different factors, both environmental and managerial and their interactions (*7*). Nitrification is the aerobic process in which ammonium (NH_4^+) is oxidized to nitrite (NO_2^-) and further oxidized to nitrate (NO_3^-) (*8*). Denitrification is an anaerobic process in which NO_3^- is reduced to N_2O and dinitrogen gas (N_2) and it is dependent upon many factors including soil pH, degree of anaerobicity of soil, soil C content, NO_3^- content and water content (*9*, *10*). The greatest rates of N_2O

emissions from soils tend to be associated with the denitrification pathway whereas nitrification-derived N_2O flux rates are smaller (*11*). However, more often than not, conditions favorable for the nitrification process tend to be more common, i.e., greater soil aeration, lower WFPS, good soil drainage and more aerobic conditions (*11*, *12*).

The addition of synthetic fertilizers is a major source of N_2O production; it is estimated that approximately 1.25% of all N fertilizer (both inorganic and organic forms) added to soils is emitted as N_2O (*1*). Nonetheless, recent reviews have shown that emissions factors can vary from 0.1 to 7.0% from both natural and agricultural soils (*13*). The production of both natural and fertilizer-derived N_2O from agricultural soils is again largely dependent upon management practices, including fertilizer and irrigation timing, microbial processes, local climate conditions and soil properties, including soil water and N dynamics, thus making the quantification of annual N_2O emissions from specific cropping systems a challenging task.

It is well documented that agriculture is a substantial source of GHG emissions worldwide, but that also a potential for GHG reductions currently exists within agriculture (*14–16*). Consequently, assessing annual emission budgets is a necessary task in order to determine the current impact that agriculture has on climate, to estimate the future potential mitigation of climate change related to anthropogenic increases of GHG's in the atmosphere, and to ensure future food security while reducing the agricultural impact on GHG concentrations in the atmosphere.

Determining annual N_2O budgets is often difficult due to the high spatial and temporal variability of N_2O fluxes (*17*). Process based biogeochemical models, such as the denitrification decomposition model (DNDC) (*18*) and the daily time step version of the CENTURY model (DAYCENT) (*19*), have been used to estimate GHG emissions by simulating crop growth and soil carbon (C) and nitrogen (N) dynamics as related to, agricultural management, soil properties, and climate. These biogeochemical models, however, still contain substantial uncertainty in their estimations of N_2O emission arising from different soil conditions and management practices across spatial and temporal scales. For the State of California, this is particularly true, due to its wide variation in soils and cropping system types. Research on the effects of both conventional and alternative management practices on N_2O emissions are lacking for California, especially for vegetable and perennial cropping systems such as vineyards and nut orchards (*20*). Furthermore, until recently there was very little ground-based field data available to quantify the interactions and impacts of irrigated farming with alternative practices on soil C and N dynamics and GHG emissions (*15*). Therefore, further research is necessary if climate change mitigation measures are to be realized in the future.

The objectives of this paper are to (1) discern the state of knowledge for factors from both alternative and conventional cropping systems that contribute to N_2O emissions from vegetable and perennial cropping systems in California, (2) evaluate current methodologies, and (3) make recommendations towards GHG mitigation strategies for Californian agriculture.

California: A Case Study

California has a wide range of climatic regions and ecosystems (e.g., croplands, forests, coastal margins, mountainous areas, and desert). California agriculture is incredibly diverse because of its varied mesoclimates that allow for a wide variety of annual (i.e., vegetables and cereals) and high-value specialty perennial crops, such as citrus, nuts, stone fruits, and wine and table grapes. California accounts for approximately 43% of the vegetable and fruit production and 42% of nut production in the United States (*21*). Despite the apparent importance of agriculture within California there is little data on GHG emissions from Californian agricultural lands (e.g., (*20*, *22*, *23*)).

California is the 10th largest emitter of GHG's in the world, accounting for approximately 493 million metric tons of CO_2 equivalents per annum (*22*). Within California, it is estimated that agricultural and forestry practices contribute to approximately 8% of the total GHG emissions, of which over 50% are accounted for by N_2O (*22*). Consequently, addressing GHG emissions reductions potentials within California agriculture is vital to developing and implementing alternative management strategies, such as conservation tillage practices, cover cropping, organic management, residue management strategies, biochar additions, reduced synthetic N fertilizer input, using improved N sources (e.g. nitrification inhibitors and poly-coated urea), and state-of-the-art irrigation systems. These practices likely provide an opportunity to reduce GHG emissions and partly address climate change issues both locally and globally. Currently agricultural management practices within California are highly intensive because the vast majority of crop acreage is cultivated using standard tillage (ST) operations, high inputs of synthetic N fertilizers, and intensive irrigation schedules (*20*).

Effects of Tillage and Cover Cropping on N_2O Fluxes

The mechanical disturbance of soil by agriculture practices, through tillage and tractor compaction of soil, significantly influences gas fluxes (*24*). Standard tillage (ST) is known to stimulate mineralization of both C and N present within soils. Furthermore, it is thought that tillage can temporarily reduce competition between plants roots and microbial communities for N and thus potentially increase N_2O emissions (*11*). In an intensively managed vegetable system in Northern California, the net mineralization of N and the accumulation of NO_3^- markedly increased for several days following standard rotor tillage operations of the soil surface, which in turn could be associated with observed higher rates of denitrification and hence greater N_2O emissions (*25*).

Over the past few decades, ST operations have decreased in favor of no-tillage or reduced tillage practices in the United States (*26*). Reducing tillage intensity has been cited as a sustainable practice because it reduces fossil fuel usage and labor needs. It also enhances certain aspects of soil quality such as reduced erosion, increased soil C content and improved water retention (*27*, *28*). Increases in soil C can also offset increases in atmospheric CO_2 (*29*), however, the interaction between tillage practices and soil conditions and their influence on other potent GHG's such as N_2O and methane (CH_4) are still inconclusive (*20*, *30*).

In California, there is a shortage of information regarding conservation tillage practices, especially within perennial systems such as vineyards that cover a huge acreage of the state's cropped land. One reason for the lack of information is the low (10%) land area where CT is supported (*31*). Consistent with other studies that have observed the initial increase in N_2O emissions under newly converted CT systems (*4*, *30*), growing season N_2O emissions from a corn-tomato system under minimum tillage following one year after conversion from standard tillage operations, were greater than those from a standard tilled corn-tomato system on a fine textured soil under California conditions (Davis, CA) (*32*). Based on the compilation of data and extensive literature review (*30*), it has been predicted that following the initial conversion of annual agricultural systems to CT from ST, N_2O emissions would decrease after several years if the practice was maintained in the long term. These studies do not include perennial ecosystems; furthermore, many model predictions and inventories have also shown a distinct lack of information for perennial systems.

In vineyard systems where cover cropping combined with CT is utilized to reduce the use of synthetic N fertilizers, cover crops can provide habitats for beneficial insects and increase soil quality and soil C (*33–36*). However, it still remains largely unknown what the effect of cover cropping and CT has upon GHG production and consumption, particularly N_2O. Increased emissions from cover cropped vineyard systems [i.e., Trios 102 (*Triticale x Triosecale*), ('Trios'), Merced Rye (*Secale cereale*)] as compared to non-cover cropped vineyards (i.e., tilled, bare soil) have been documented in California (Monterey County; (*37*)). Nonetheless, this is only one study and so making any future generalizations regarding the effect of CT and cover crops on N_2O emissions from vineyards needs to be done cautiously. A more recent study (*38*) assessed direct N_2O emissions following the transition from ST to CT in a cover cropped Northern California vineyard over a single growing season. Using static closed chambers, frequent measures of N_2O were completed both in the vine and tractor row following significant management events, such as irrigation, fertilization, and cover crop mowing and incorporation, as well as weather events such as precipitation. Measurements lasted a full seven to ten days following irrigation, fertilization, precipitation or vineyard floor management events respectively (*38*). Cumulative N_2O emissions in the CT system were 0.19 ± 0.017 kg N_2O-N ha^{-1} $season^{-1}$ in the vine row and 0.11 ± 0.018 kg N_2O-N ha^{-1} in the tractor row and were greater, but not significantly, compared to 0.13 ± 0.021 kg N_2O-N ha^{-1} in the vine row and 0.07 ± 0.041 kg N_2O-N ha^{-1} in the tractor row of the ST system (*38*) (Figure 1). Compared to other studies of irrigated agricultural systems in similar Mediterranean climates, the total cumulative emissions for the vineyard were much lower primarily due to the relatively small amount of N fertilizer added (5 kg N ha^{-1} $season^{-1}$) and the drip irrigation system, which results in high N and water use efficiency and thus reduced N_2O emissions (*38*). Moreover, fertilization even at such low amounts still had the largest impact upon N_2O emissions under vine rows over the growing season, while cover crop mowing and residue incorporation had the greatest influence within tractor rows (Figure 2). Hence, management events play a significant role in N_2O emissions from vineyards (*37*, *38*).

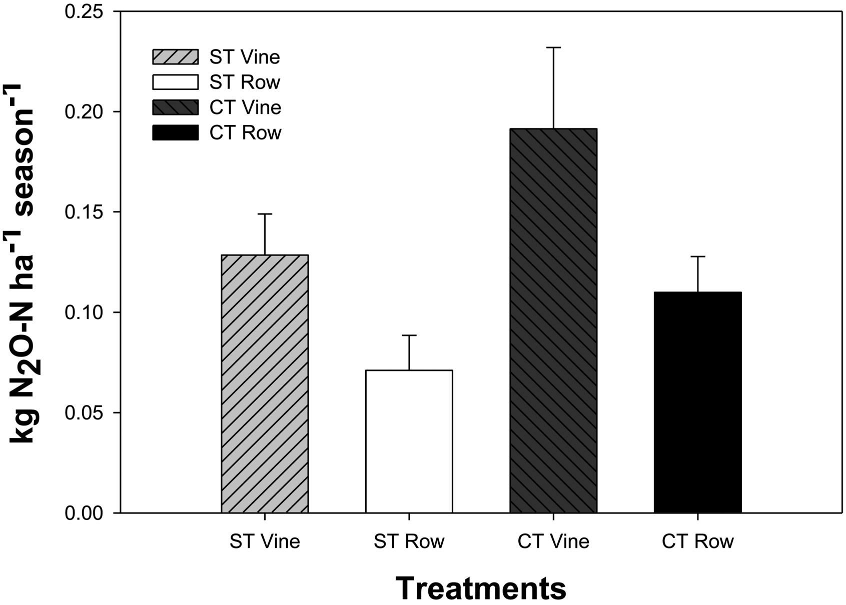


Figure 1. Total seasonal N_2O emissions from a) standard tillage (ST) vine b) standard tillage (ST) row c) conservation tillage (CT) vine and d) conservation tillage (CT) row. Error bars represent the standard error between replicates (34).

Unfortunately in order to reliably predict future GHG emissions from vineyards and other perennial crops within California and to develop future best management practices to reduce emissions and sustain future crop production practices, longer term studies and the influence of winter precipitation patterns are needed to estimate accurate and complete budgets of N_2O within California cropping systems.

Irrigation and Fertilization Effects on N_2O Fluxes

Two of the main limiting factors affecting agricultural crop production within arid and semi-arid regions are water and N. Both of these factors are intrinsically linked to the production of N_2O emissions from soils in agricultural ecosystems. Irrigation not only stimulates plant growth, which in turn can enhance C storage in soils through increases in yields (*15*), but it can also accelerate microbial turnover of C and N (*39*), thereby increasing the potential for N_2O production. Many studies have assessed net N_2O fluxes under different cropping systems (*13*), and it has been shown that there is a strong relationship between irrigation and the stimulation of N_2O production (*40*). However, limited data is available for irrigated agriculture for such diverse regions like California where there are many different types of irrigation systems utilized within the various cropping systems of California (*41*).

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

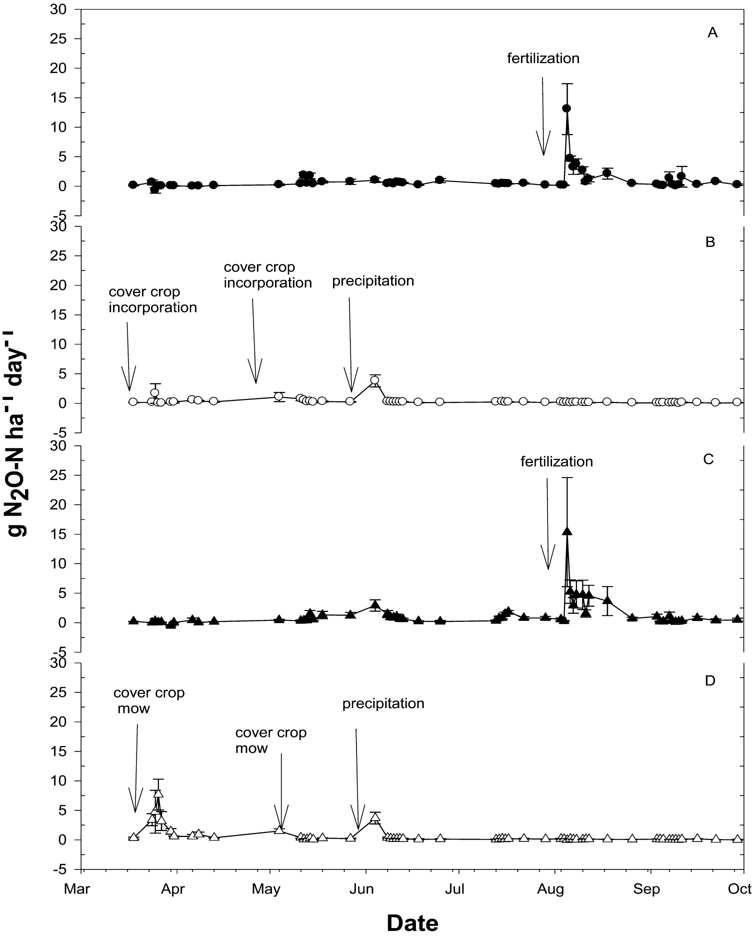


Figure 2. Seasonal N_2O flux rates from a) standard tillage (ST) vine b) standard tillage (ST) row c) conservation tillage (CT) vine and d) conservation tillage (CT) row. Error bars represent the standard error between replicates (34).

Of the 5023 Mha dedicated to global agriculture, where approximately 28% is devoted to cropland (1405 Mha) (*42*) 18% of the total, receives additional water through irrigation (*43*). In the semi-arid and arid climate of California, where evaporative demands are high and the annual precipitation is low to non-existent during the hot summer growing season, irrigation is essential to maintain adequate crop yields. Approximately 76% of the total cropland area within California is currently under irrigation (*44*). In semi-arid and arid regions, like those observed in California, the soils are often low in available nutrients and have low microbial activity when dry (*45*, *46*). However, following soil moistening, especially after irrigation events, the microbial population within the soil greatly increases and N mineralization takes place at a rapid rate (*47*, *48*). Furthermore, after irrigation and soil water saturation, anaerobic micro sites can occur through the high rate of oxygen consumption from intense microbial respiration when oxygen demands exceed supply (*49*). This supports the microbial process of denitrification, but only if there is sufficient organic C and NO_3^- available (*8*, *17*). In addition, these wet-dry cycles that often accompany irrigation events are known to affect soil microbial processes and subsequently C and N cycling, as well as the diffusivity of soil gases, which regulate both the production and consumption of N_2O between the soil and atmosphere interfaces (*50*), and thus strongly influences both nitrification and denitrification rates of N_2O from the soil.

When N_2O emissions were measured from irrigated tomato crops within California's Central Valley, elevated N_2O emissions following irrigation during the cropping season occurred when WFPS was above 60% through the process of denitrification (*40*). This is consistent with previous studies which show that denitrification becomes a highly significant source of N_2O once soils have exceeded field capacity or have a WFPS in the range of 60-90% (*9*, *51–53*). The elevated N_2O emissions lasted for two days following the wetting event and declined as the top 15 cm of the soil surface dried out quickly (*40*). During the cropping season, N_2O was clearly controlled by irrigation and evapotranspiration (drying) rates, especially in quickly drying soils. In a California vineyard (Monterey County), N_2O emissions were measured after N fertilization (31.8 kg N ha^{-1}; ammonium nitrate urea solution 32-0-0: 45.2%NH_4NO_3 and 34.8% urea by weight) using a drip system (fertigation) within the vine row. The soil that received herbicide to control weed cover over a five year period had greater N_2O emissions over a 3-day period than the soil that was cultivated for the same duration (*54*). The cultivated soil had slightly greater organic matter content and microbial biomass than the herbicide treated soil, suggesting that greater weed presence in the cultivated soil contributed to greater N retention due to inorganic N uptake by the weeds. Furthermore, we suggest that the greater presence of weeds in the cultivated soils also provided labile soil C substrates that could facilitate greater conversion of N_2O to N_2 (*55*).

It is important to predict the impact of irrigation practices on soil N turnover and mineralization as well as to optimize management practices in order to reduce the losses of N to the environment. In California, four major types of irrigation (i.e. flood, (including furrow), surface drip, micro-sprinkler and sub-surface drip irrigation) are utilized. Alternative and sustainable management practices are being advocated with increasing political pressures to reduce and mitigate GHG emissions from agriculture. The use of sub-surface drip (SSD) over surface drip (SD) or micro-sprinkler (MS) irrigation has been postulated to be the most efficient irrigation practice with a great potential to reduce water usage, increase nutrient efficiency and to reduce both N_2O and CO_2 emissions (*56*). The SSD technology is an improvement over SD irrigation, where the water needs of the crop can be met and delivered to the root system directly in a timely manner with minimum losses (*57*). Many of California's fruit and nut growers are already implementing more efficient irrigation systems such as SD and MS over flood and furrow. There is also a trend for growers to switch from lower value field crops to the more high value specialty crops such as almonds and wine grapes, of which the former used to be irrigated using flood or furrow (*58*). A Central Valley study in a split plot tomato field trial that compared the effect of SSD or furrow irrigation on event based N_2O emissions with or without a winter legume cover crop, observed that SSD decreased N_2O emissions by half compared to the furrow irrigation regardless of the presence or absence of a winter cover crop (*41*). Despite this, there is still little to no data related to the effect of irrigation type on N_2O emission from soils in California perennial systems. One short-term study (Figure 3) shows the diurnal pattern of N_2O following 36 hours after an irrigation event where no fertilizer was added to a Northern California almond orchard. The almond orchard was situated in Colusa County at the Nickels Soil Laboratory where three different irrigation systems, SD, MS and SSD, were utilized; static closed chambers were placed directly under the irrigation systems in the tree row as well as in the tractor row in order to obtain representative fluxes occurring from soil wetting. Diurnal fluctuations in emissions are often attributed to fluctuation in soil temperatures. However, there was no significant diurnal pattern observed within the almond study, most likely due to the high spatial variability of the replicates within the field (*59*). Nevertheless, N_2O emissions did vary over the 36 hour time period following irrigation, thus highlighting the high degree of variability in N_2O emissions over relatively small time scales and demonstrating the importance of consistent measurements over a similar time of day in order to measure representative fluxes for the system. The SSD irrigation system led to lower emissions on the whole compared to SD and MS irrigation treatments, which corroborates previous research showing that SSD is a highly efficient irrigation system that is precise at delivering water directly beneath the crop roots to a relatively small area. By doing so, SSD restricts microbial activity (*41*) and anaerobic microsite development, thereby limiting denitrification (*17*). The SD and MS irrigation practices led to slightly higher N_2O fluxes due to the greater delivery of water to the soil and, therefore, surplus of water.

Fertigation is a more effective and cost-saving way of supplying a crop with its nutrient needs and provides flexibility in the fertilization practice since fertilizers can be added directly to the active crop root zone (*60*). Emissions of N_2O were measured for four days after 50 kg N ha^{-1} in the form of urea nitrate (UN 32) was added to the Nickels Soil Laboratory almond orchard in California through three different irrigation systems (SD, MS and SSD) (Figure 4). The SD irrigation system emitted greater fluxes of N_2O compared to both the MS and SSD systems within the tree row. Generally, in the zone directly under the SD emitter, localized anaerobic conditions can occur following an irrigation event (*61*). Such anaerobic conditions will reduce the oxygen in the soil and thus provide optimum conditions for denitrification. A previous study (*62*) observed during SD irrigation increased NH_4^+ concentrations in soils due to mineralization of partially dried soils; in turn NO_3^- decreased as soils saturated following irrigation and was thought to be lost as N_2O or N_2 due to the more anaerobic soil conditions. For the Nickels almond study, emissions were most likely produced through the denitrification process, as surface applied urea is expected to stimulate more denitrifying activity within the upper soil layers (*62*).

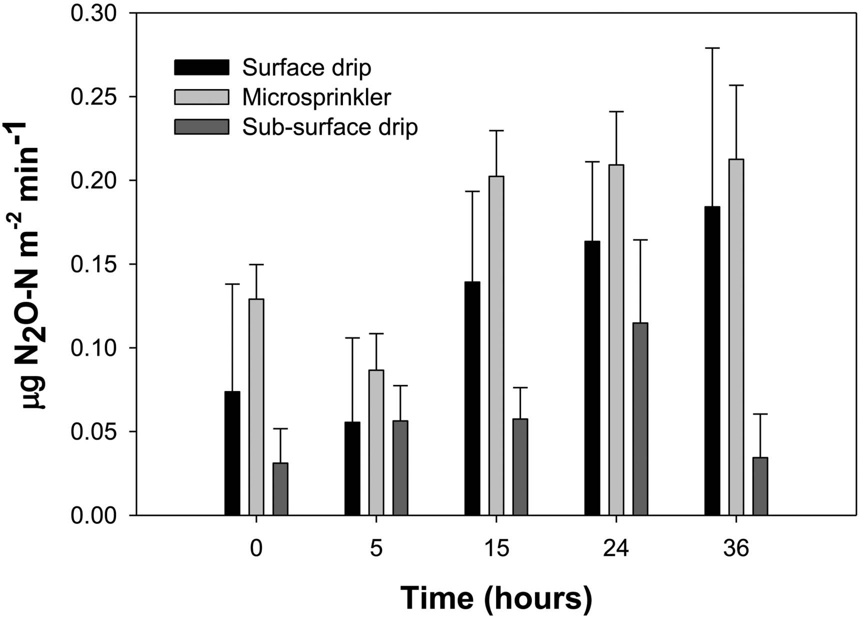


Figure 3. Diurnal changes in N_2O emissions from three different irrigation systems in a Northern California almond orchard following 36 hours after irrigation without fertilization. Error bars represent standard error of the mean (n=4).

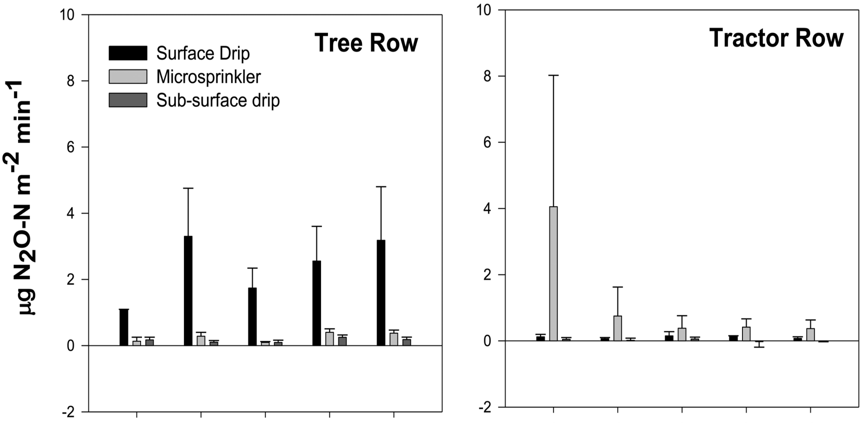


Figure 4. N_2O emissions for four days following N fertigation of urea nitrate (UN32) in both the tree and tractor rows of a Northern California almond orchard. Error bars represent standard error of the mean (n=4).

Previous research has shown that the evolution of a N_2O peak following a management event such as fertigation tends to be relatively short-lived, lasting only a couple of days to a couple of weeks (*11*). N_2O emissions after the four days following the fertigation event in the almond orchard were still elevated in the SD irrigation treatment, indicating that future studies should continue with field measurements until the N_2O flux returns to background levels to ensure complete measurements of the peak flux and improve accuracy of annual budgets. Total cumulative emissions over the four day period were observed to be significantly lower in the SSD system compared to the other two irrigation treatments (Figure 5). Congruent with earlier studies, SSD is a highly efficient irrigation method which limits the losses of N fertilizers (*56*) and reduces N_2O emissions from soils leaving less N available to be transformed to N_2O by microbial processes (*41*).

The adoption of SSD irrigation systems within California is slow and represents less than 15% of all irrigation systems utilized within California (*41*). SSD irrigation requires maintenance and can be costly at initial installation. However, SSD has demonstrated the capacity to reduce N_2O emissions, and with the increased nutrient and water use efficiency the method provides, future adoption should be considered in perennial crops.

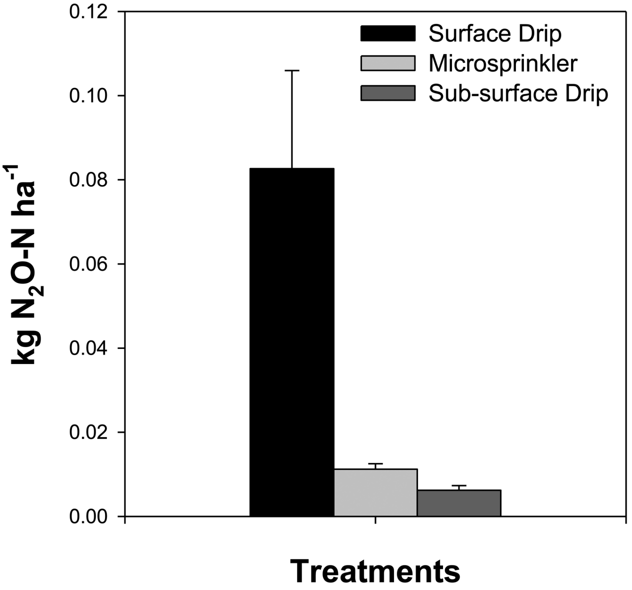


Figure 5. Cumulative emissions from a fertigation event under three different irrigation systems within a Northern California almond orchard. Error bars represent the cumulative error of the mean (n=4).

Soil Amendments and Residue Management

In agriculture the use of organic amendments (e.g. manures, composts and mulches) can lead to the accumulation of soil organic carbon (SOC) by improving aggregation, reducing the need for synthetic N fertilizer additions and simultaneously providing crops with adequate nutrients. Nethertheless, in agricultural soils, inputs of N from fertilization, composts, manures, post harvest residues or similar soil amendments are major contributors to N_2O emissions (*63*, *64*). Emissions of N_2O have been found to be greater when the amendment or residue has a lower C:N ratio (*63*, *65*, *66*), leading not only to increases in N_2O emissions but also fast rates of NO_3^- leaching (*67*). Conversely, previous studies have reported that many factors can complicate the relationship between residue input and N_2O fluxes (*68*). The main confounding factors are crop type, the biogeochemical composition of the residue and amendment, tillage regimes, soil moisture, pH, climate and the time of year residue was incorporated (see review (*68*)).

In light of future mitigation of climate related changes through increases in GHG emissions to the atmosphere, the use of pyrolyzed biomass, termed biochar, as a soil amendment has recently been reported to have beneficial effects by improving soil quality, increasing C sequestration and potentially reducing N_2O emissions from soils (*69–71*). Biochar is produced when green wastes, such as orchard pruning's and nut shells, are gasified in the absence of oxygen in a process termed pyrolysis. The pyrolysis process produces a renewable energy source from the biomass itself in the form of a gas or other byproducts (e.g. bio-oil) which can be used instead of fossil fuels. The addition of biochar produced from green waste biomass into agricultural soils, may provide a significant terrestrial sink of C in soils, enhance soil quality, reduce greenhouse gas emissions, and provide an environment which promotes a healthy soil food web.

Previous research has indicated a decrease in N_2O emissions following the application of biochar to soils (*72*, *73*). In a short term, small field scale study in a lettuce crop production system in Yolo County, California, biochar derived from a high temperature (950 ^oC) gasification pyrolysis of waste walnut shells was applied to the soil (Figure 6). The treatments included a control (no amendment), compost (5 t ha^{-1}), and biochar (5 t ha^{-1}). All treatments received fertilizer (250 kg N ha^{-1}) in pellet form and were subject to surface drip irrigation. N_2O emissions were measured daily (Figure 6) using the static closed chamber method until the lettuce was ready to harvest. Total cumulative emissions over the whole experiment were highest from the compost plots (Figure 7). Compost can increase C availability and the soil anaerobicity when the porosity of the compost amended soil is low, and has a relatively small particle size (*74*), thus enhancing the potential to release N_2O through denitrification pathways compared to non-compost amended soils (*75*). Furthermore, the addition of C from the compost amendment would be more readily available for utilization by micro-organisms compared to the biochar amendment, which would increase denitrification rates and subsequently increase in emissions of N_2O (*76*).

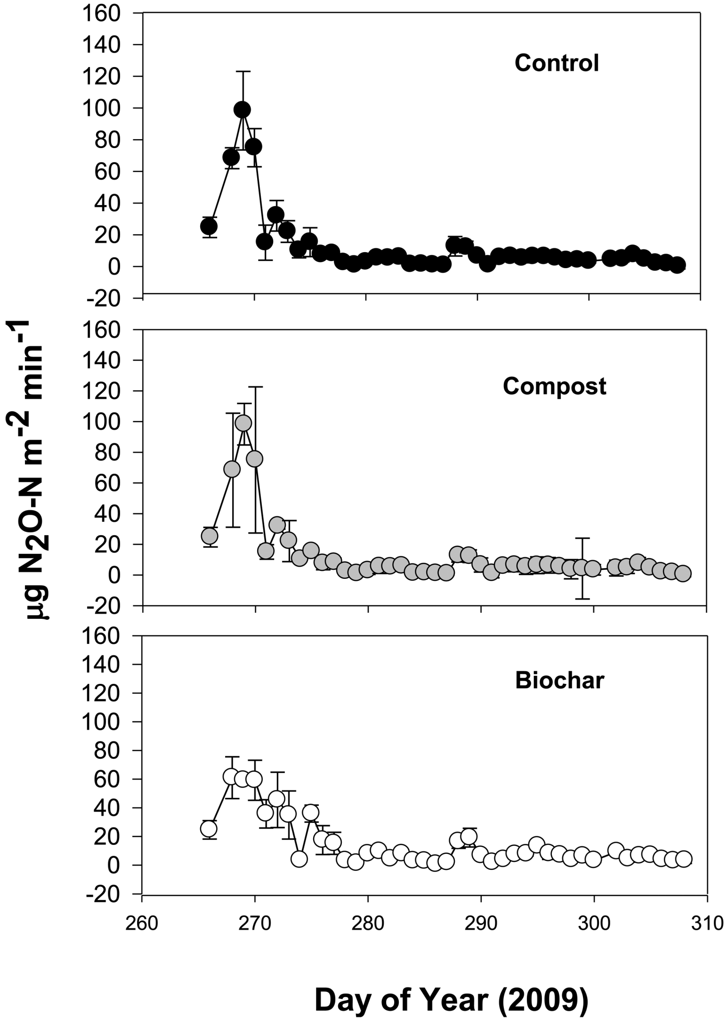


Figure 6. N_2O emissions following the application of 5 t/ha high temperature (950 °C) walnut shell biochar or compost amendments to small field plots following a lettuce rotation.

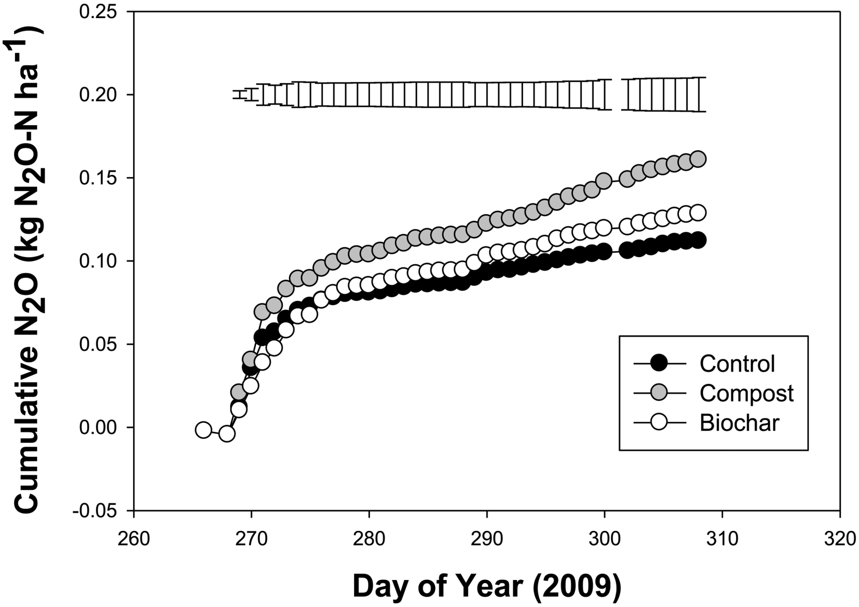


Figure 7. Cumulative N_2O emissions following the application of biochar or compost to soil under lettuce. Error bars represent the standard cumulative error of the mean for the three treatments.

N_2O emissions were significantly reduced by approximately 41% in biochar amended soils during the initial N_2O peak after fertilization as compared to compost and control plots (Figure 6). The N_2O emissions may have been reduced in the biochar amended soils due to the possible adsorption and retention of NH_4^+ in the soil through increased oxidative reactions on the biochar surface, thus reducing the amount of N available for nitrification and denitrification (*71*, *77*). Despite the obvious reduction in N_2O in biochar plots at the start of the experiment, cumulative emissions (Figure 7) were not significantly different from control plots, but were lower than compost amended soils. The N_2O emissions following the application of biochar to soils is still relatively understudied and data is contradictory depending upon biochar feedstock and the interactions of local soil conditions with rates of biochar application (*77*). For instance, a previous and contrasting study (*71*) observed that, following the application of biochar, N_2O fluxes were inconsistent, variable and appearing to increase early within the experiment as compared to controls. However, as the experiment progressed, reductions in emissions of N_2O were most likely due to the increased aging of the biochar soil surface, thus increasing the capacity for the biochar to absorb available N in the soils (*71*). The potential for this new technology to be applied to agricultural soils is still in its infancy, requiring future research to ensure that the application of biochar does have the capacity to reduce N_2O emissions, or at least not increase N_2O emissions.

Methodology Evaluation

Despite the numerous studies investigating N_2O emissions from agricultural ecosystems and the controlling environmental and management factors, it is still difficult to predict and constrain future emissions under field conditions. This is primarily due to the facts that microbial processes of denitrification and nitrification have very specific optimum conditions that change both spatially and temporally within the soil, and that there is a high uncertainty in N_2O monitoring data related to the quality and quantity of field measurements. Many studies have only measured N_2O fluxes from the field level either weekly or biweekly, while some studies have measured the fluxes more intensively by measuring either once per day or every couple of days with more frequent sampling occurring over periods where management events such as fertilization occurs (*78*). The difference in sampling frequency can increase uncertainty and reliability of estimates of N_2O emissions occurring from agricultural soils (*79*). For example, a previous study (*80*) observed a 20% overestimation in total annual emissions from sampling done on a weekly basis as opposed to total emissions calculated on a daily basis. Consequently, the lack of intensive data and the resulting substantial uncertainty around estimates of N_2O emissions for the major irrigated crops in California is definitely a pressing issue that needs to be resolved. .

N_2O fluxes are commonly determined through the static closed chamber field technique, which is utilized in research primarily due to the relative simplicity and ability to allow process based studies of N_2O (*81*). A significant problem associated with this technique is the relatively small area of the soil surface covered by a single chamber. This renders extrapolation to whole field scale difficult due to the high spatial variability associated with N_2O emissions (*82*). In order to ameliorate this issue, the number of static chambers employed at each field site would need to be increased. Furthermore, in order to constrain accurate and reliable N_2O budgets, measurements need to be taken more frequently, especially during management and precipitation events that greatly influence N_2O fluxes. This will facilitate the assessment of precise N_2O emission patterns crucial for the calibration and validation of process based biogeochemical models needed to dependably predict annual N_2O emission budgets. Consequently, the full characterization of N_2O fluxes from agricultural soils in California requires a great effort spatially, and with near continuous field measurements similar to those conducted in previous studies (*83*, *84*); this effort becomes a laborious and expensive, but very necessary, endeavor.

Previously reported coefficients of variation for N_2O fluxes from agricultural soils have ranged from 100-900% (*85*), -40-70% (*13*, *86*) and -30-300% (*87*), thus showing the great variation within agriculture. Given the lack of data for California crops, the studies presented within this paper are a first contribution to the data pool for N_2O emissions occurring from perennial crops within California. The study by Garland *et al* (*38*) clearly shows the high temporal variability over a single growing season in a Northern Californian vineyard and highlights the N_2O peak evolution following significant management events such as tillage and fertilization. Furthermore, this study provides a more fundamental understanding of the effects of alternative management strategies on N_2O emissions that may not have been realized if measurements were less frequent. The Garland *et al* (*38*) study and others (*37*, *54*) are instrumental in reducing the uncertainty and variation surrounding N_2O fluxes from agriculture.

We have also demonstrated that not only are N_2O emissions highly variable over a seasonal timescale, emissions are also highly variable on the much smaller diurnal time scale. N_2O fluxes from Nickels Soil Laboratory almond orchard varied greatly over a 36 hour time period. A future recommendation for N_2O research would be to monitor N_2O fluxes over shorter timescales and multiple times a day, especially during times of intensive management and weather events. This of course would require a huge manual effort; therefore deployment of automated static chambers with the ability to sample multiple times a day for extended time periods are one option to monitor diurnal changes in N_2O emissions from agricultural soils. In addition, other techniques such as micro-meteorological methods have a large spatial footprint and can be employed to monitor near continuous observation in time (*88*). Both techniques require expensive equipment for data collection and analysis.

Potential Mitigation Measures

Currently a variety of mitigation options exist to reduce GHG emissions occurring from agricultural soils. Improvements to agronomic practices such as N fertilization, nutrient and water use efficiency (e.g. use of reclaimed municipal waste water), and residue management (e.g. green manures) represent the major mitigation options to reduce GHG's. Furthermore, the use of enhanced-efficiency N fertilization techniques, such as nitrification inhibitors and poly coated urea, are also potential mitigation options; they have been shown to reduce N_2O emissions by almost 40% (*89*) compared to conventional N fertilizers such as urea (*90*, *91*). However, there is still a lack of data for many of the mitigation options available within California agriculture and it is still challenging to predict the interactions between mitigation options under specific field conditions in California. Therefore, we suggest that potential practices must be evaluated first on an individual basis in order to understand the change in management and land-use with interactions within local soil conditions. Subsequently, mitigation options should also be assessed in combination to ensure that one mitigation strategy paired together with another practice does not enhance emissions. It therefore seems appropriate that a mixture of mitigation management options would be better to constrain emissions from agriculture.

Process based biogeochemical models combined with field based measurements will be able to evaluate future scenarios and management options best for reducing GHG's. Furthermore, a whole system based approach that evaluates the overall long term production viability goals of the crop in conjunction with GHG reduction goals is the way forward in order to adapt and mitigate climate change and to maintain future food security and agricultural sustainability. The data presented within this paper supports the suggestion that both environmental and soil conditions in conjunction with agricultural management practices are critical in controlling the release of N_2O from

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

agricultural soils in California. Water and N are clearly two of the most important factors affecting N_2O emissions; therefore, an improvement in N fertilizer and irrigation efficiency is needed. The type and placement of N fertilizers deeper within the soil layer using SSD irrigation, reducing unnecessary irrigations, and using controlled timing of irrigations while satisfying minimum crop N and water requirements to maintain sufficient yields and quality are potential mitigation options that will reduce N_2O emissions (*5*, *92*, *93*). Furthermore, the addition of biochar to soils could also reduce atmospheric concentrations of CO_2 through C sequestration in soils as well as mitigating N_2O produced from soils, while enhancing crop productivity and improving soil quality.

Conclusion

This paper highlights both the high degree of spatial and temporal variability of N_2O emissions from agricultural soils in California and the significant influence of management (e.g., irrigation and fertilization) upon these emissions. Despite the current emerging data for California, there is still an urgent need to collect more frequent measurements. Furthermore, integration of all methods of collection, reporting and modeling in order to reduce uncertainty around estimates of N_2O emissions is pertinent. Agricultural mitigation measures must also be in cohesion with other sociological and economic development strategies to succeed. Not only the reduction in GHG emission should be taken into account when assessing alternative and conservation management practices, as most of these practices have associated co-benefits (e.g. reduced costs, improved soil health, enhanced biodiversity) that are also highly valuable in their own right and will be necessary for the future sustainability of California agriculture. There is a great potential for California agriculture to reduce GHG emissions and be involved in the future development and implementation of alternative management practice. However, all alternative practices must also be evaluated for any potential negative impacts such as reduced yields and crop quality. Also, if California is to succeed in meeting its climate change and GHG reduction goals there is a definite need for a synergy to exist between current technologies and socio-economic sectors and pave the way for forthcoming policies to effectively tackle the complex issue of climate change.

Acknowledgments

We acknowledge support from the California Energy Commission, the Kearney Foundation of Soil Science and the Almond Board of California for this work.

References

1. Barker, T.; Bashmakov, I; Bernstein, L.; Bogner, J. E.; Bosch, P. R.; Dave, R.; Davidson, O. R.; Fisher, B. S.; Gupta, S.; Halsnæs, K.; Heij, G. J.; Kahn Ribeiro, S.; Kobayashi, S.; Levine, M. D.; Martino, D. L.; Masera, O.; Metz, B.; Meyer, L. A.; Nabuurs, G. J.; Najam, A.; Nakicenovic, N.; Rogner, H. -H.; Roy, J.; Sathaye, J.; Schock, R.; Shukla, P.; Sims, R. E. H.; Smith, P.; Tirpak, D. A.; Urge-Vorsatz, D.; Zhou, D. Technical Summary. In: *Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Metz, B., Davidson, O. R., Bosch, P. R., Dave, R., Meyer, L. A., Eds.; Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA, 2007.
2. Robertson, G. P. Fluxes of nitrous oxide and other nitrogen trace gases from intensively managed landscapes: a global perspective. In *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*; Harper, L. A., Mosier, A. R., Duxbury, J. M., Rolston, D. E.; American Society of Agronomy: Madison, WI, USA, 1993, pp 5−108.
3. Crutzen, P. J. Upper limits on atmospheric ozone reductions following increased application of fixed nitrogen to the soil. *Geophys. Res. Lett.* **1979**, *3*, 169.
4. Del Grosso, S. J.; Parton, W. J.; Mosier, A. R.; Walsh, M. K.; Ojima, D. S.; Thornton, P. E. DAYCENT national-scale simulations of nitrous oxide emissions from cropped soils in the United States. *J. Environ. Qual.* **2006**, *35*, 1451–1460.
5. Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; Van Dorland, R.. Changes in Atmospheric Constituents and in Radiative Forcing. *In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA, 2007.
6. Mosier, A.; Kroeze, C.; Nevison, C.; Oenema, O.; Seitzinger, S.; van Cleemput, O. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutr. Cycl. Agroecosys.* **1998**, *52*, 225–248.
7. Williams, E. J.; Hutchingson, G. L.; Fehsenfeld, F. C. NO_X and N_2O Emissions from Soil. *Global Biogeochem. Cycles* **1992**, *6* (4), 351–388.
8. Paul, E. A.; Clark, F. E. Soil microbiology and biochemistry; Academic Press: London, 1996; pp 340.
9. Schjønning, P.; Thomsen, I. K.; Moldrup, P.; Christensen, B. T. Linking soil microbial activity to water- and air-phase contents and diffusivities. *Soil Sci. Soc. Am. J.* **2003**, *67*, 156–165.

10. Dalal, R. C.; Want, W.; Robertson, G. P.; Parton, W. J. Nitrous oxide emission from Australian agricultural lands and mitigation options: a review. *Aust. J. Soil Res.* **2003**, *41*, 165–195.
11. Skiba, U.; Smith, K. A. The control of nitrous oxide emissions from agricultural and natural soils. *Chemosphere* **2000**, *2*, 379–386.
12. Venterea, R. T.; Rolston, D. E. Mechanisms and kinetics of nitric and nitrous oxide production during nitrification in agricultural soil. *Glob. Change Biol.* **2000**, *6*, 303–316.
13. Bouwman, A. F.; Boumans, L. J. M.; et al. Emissions of N_2O and NO from fertilized fields: Summary of available measurement data. *Global Biogeochem. Cycles* **2002**, *16* (4).
14. Cole, C. V.; Flach, K.; Lee, J.; Sauerbeck, D.; Stewart, B. Agricultural sources and sinks of carbon. *Water, Air, Soil Pollut.* **1993**, *70* (1-4), 111–122.
15. Follet, R. F. Soil management concepts and carbon sequestration in cropland soils. *Soil Tillage Res.* **2001**, *61*, 77–92.
16. Jawson, M. D.; Shafer, S. R.; Franzluebbers, A. J.; Parkin, T. B.; Follett, R. F. GRACEnet: Greenhouse gas reduction through agricultural carbon enhancement network. *Soil Tillage Res.* **2005**, *83*, 167–172.
17. Christensen, S.; Simkins, S.; Tiedje, J. M. Temporal patterns of soil denitrification; their stability and causes. *Soil Sci. Soc. Am. J.* **1990**, *54*, 1614–1618.
18. Li, C; Frolking, S; Harriss, R Modeling carbon biogeochemistry in agricultural soils. *Global Biogeochem. Cycles* **1994**, *8*, 237–254.
19. Del Grosso, S. J; Parton, W. J.; Mosier, A. R.; Hartman, M. D.; Brenner, J.; Ojima, D. S; Schimel, D. S Simulated interaction of carbon dynamics and nitrogen trace gas fluxes using the DAYCENT model. In *Modeling Carbon and Nitrogen Dynamics for Soil Management*; Schaffer, M., Ma, L., Hansen, S., Eds.; CRC Press: Boca Raton, Florida, 2001; pp 303−332.
20. Suddick, E.; Scow, K. M.; Horwath, W. R.; Jackson, L. E.; Smart, D. R.; Mitchell, J. P.; Six, J. The potential for California soils to sequester carbon and reduce greenhouse gas emissions: A holistic approach. *Advances in Agronomy*; Academic Press: Burlington, 2010; Vol. 107, pp 123−162.
21. California Farm Bureau Federation (CFBF). (2002). News division, http://www.cfbf.com.
22. Bemis, G.; Allen, J. Inventory of California Greenhouse Gas Emissions and Sinks: 1990 to 2002 Update. *California Energy Commission (CEC) Publication*, 2005, CEC-600-2005-025.
23. De Gryze, S.; Albarracin, M. V.; Catalá-Luque, R.; Howitt, R. E.; Six, J. Modeling shows that alternative soil management can decrease greenhouse gases. *Calif. Agric.* **2009**, 84–90.
24. Linn, D. M.; Doran, J. W. Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Sci. Soc. Am. J.* **1984**, *48*, 1267–1272.
25. Jackson, L. E.; Calderon, F. J.; Steenwerth, K. L.; Scow, K. M.; Rolston, D. E. Responses of soil microbial processes and community structure to tillage events and implications for soil quality. *Geoderma* **2003**, *114* (3-4), 305–317.

26. Post, W. M.; Izaurralde, R. C.; Jastrow, J. D.; McCarl, B. A.; Amonette, J. E.; Bailey, V. L.; Jardine, P. M.; West, T. O.; Zhou, J. Enhancement of carbon sequestration in U. S. soils. *Bioscience* **2004**, *54*, 895–908.
27. Lal, R. Global potential of soil carbon sequestration to mitigate the greenhouse effect. *Crit. Rev. Plant Sci.* **2003**, *22* (2), 151–184.
28. Mitchell, J. P.; Klonsky, K.; Shrestha, A.; Fry, R.; DuSault, A.; Beyer, J.; Harben, R. Adoption of conservation tillage in California: current status and future perspectives. *Aust. J. Exp. Agric.* **2007**, *47*, 1383–1388.
29. Paustian, K.; Six, J.; Elliott, E. T.; Hunt, H. W. Management options for reducing CO_2 emissions from agricultural soils. *Biogeochemistry* **2000**, *48*, 147–163.
30. Six, J.; Ogle, S. M.; Breidt, F. J. The potential to mitigate global warming with no-tillage management is only realized when practiced in the long term. *Global Change Biol.* **2004**, *10*, 155–60.
31. Howarth, W. R.; Mitchell, J.; Six, J. Tillage and crop management effects on air, water and soil quality in California. *Conservation Tillage Workgroup Publication* **2006**, 1–8.
32. Kong, A. Y. Y.; Fonte, S. J.; van Kessel, C.; Six, J. Transitioning from standard to minimum tillage: Trade-offs between soil organic matter stabilization, nitrous oxide emissions, and N availability in irrigated cropping systems. *Soil Tillage Res.* **2009**, *104*, 256–262.
33. Bugg, R. L.; Horwath, W.; Six, J.; Van Horn, M. Practical Soil Ecology. In *Cover Crops For Vegetable Farming Systems*; Smith, R., Gaskell, M. L., Bugg, R. L., Daugovish, O., Van Horn, M., Eds.; University of California Agriculture and Natural Resources, 2007, 8000 Series.
34. Sainju, U. M.; Singh, B. P.; Whitehead, W. F. Long-term effects of tillage, cover crops, and nitrogen fertilization on organic carbon and nitrogen concentrations in sandy loam soils in Georgia, USA. *Soil Till. Res.* **2007**, *63*, 167–179.
35. Auburn, J. S.; and Bugg, R. An information data base on cover crops. In *Cover Crops for Clean Water*; Hargrove, W. L., Ed.; Soil and Water Conservation Society: Ankeny, IA, 1991.
36. Baumgartner, K.; Steenwerth, K.; Veilleux, L. Cover-Crop Systems Affect Weed Communities in a California Vineyard. *Weed Science* **2008**, *56*, 596–605.
37. Steenwerth, K.; Belina, K. M. Cover crops and cultivation: Impacts on soil N dynamics and microbiological function in a Mediterranean vineyard agroecosystem. *Appl. Soil Ecol.* **2008**, *40*, 359–369.
38. Garland, G. M.; Suddick, E. C.; Burger, M.; Horwath, W. R.; Six, J. Direct N_2O emissions following transition from conventional till to no-till in a cover cropped Mediterranean vineyard (*Vitis vinifera). Agric., Ecosyst. Environ.* **2011**.
39. Davidson, E. A. Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. In *Microbial production and consumption of greenhouse gases: Methane, nitrogen oxides, and halomethanes*. Rogers, J. E.,Whitman, W. B., Eds.; American Society for Microbiology: Washington, DC, 1991; pp. 219−235.

40. Burger, M.; Jackson, L. E.; Lundquist, E. J.; Louie, D. T.; Miller, R. L.; Rolston, D. E.; Scow, K. M. Microbial responses and nitrous oxide emissions during wetting and drying of organically and conventionally managed soil under tomatoes. *Biol. Fertil. Soils* **2005**, *42*, 109–118.
41. Kallenbach, C. M.; Rolston, D. M.; Horwath, W. R. Cover cropping affects soil N_2O and CO_2 emissions differently depending on type of irrigation. *Agric., Ecosyst. Environ.* **2010**, *137*, 251–260.
42. FAOSTAT, 2006. Agricultural data.
43. Millennium Ecosystems Assessment, 2002.
44. USDA Economic Research Service Fact Sheet, California, updated 9/10/10.
45. Vlek, P. L. G.; Fillery, I. R. P.; Burford, J. R. Accession transformation, and loss of nitrogen in soils of the arid region. *Plant Soil* **1981**, *58*, 133–175.
46. Steenwerth, K. L.; Pierce, D. L.; Carlisle, E. A.; Spencer, R. G.; Smart, D. R. A Vineyard Agroecosystem: Disturbance and Precipitation Affect Soil Respiration under Mediterranean Conditions. *Soil Sci. Soc. Am. J.* **2010**, *74*, 231−239.
47. Sanchez, P. A. Properties and Management of Soils in the Tropics; Wiley: New York, 1976; p 618.
48. Appel, T. Non-biomass soil organic N - the substrate for N mineralization flushes following soil drying-rewetting and for organic N rendered $CaCl_2$-extractable upon soil drying. *Soil Biol. Biochem.* **1998**, *30*, 1445–1456.
49. Tiedje, J. M.; Sexstone, A. J.; Parkin, T. B.; Revsbech, N. P.; Shelton, D. R. Anaerobic processes in soil. *Plant Soil* **1984**, *76*, 197–212.
50. Firestone, M. K.; Davidson, E. A. Microbiological basis of NO and N_2O production and consumption in soil. In *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*; Andreae, M. O., Schimel, D. S., Eds.; John Wiley & Sons: Chichester, 1989; pp 7−21.
51. Davidson, E. A.; Swank, W. T. Environmental parameters regulating gaseous nitrogen losses from two forested ecosystems via nitrification and denitrification. *Appl. Environ. Microbial.* **1986**, *52*, 1287–1292.
52. Dobbie, K. E.; McTaggart, I. P.; Smith, K. A. Nitrous oxide emissions from intensive agricultural systems: Variations between crops and seasons, key driving variables, and mean emission factors. *J. Geophys. Res.* **1999**, *104*, 26,891–899.
53. Sehy, U.; Ruser, R.; Munch, J. C. Nitrous oxide fluxes from maize fields: relationship to yield, site-specific fertilization, and soil conditions. *Agr. Ecosyst. Environ.* **2003**, *99*, 97–111.
54. Steenwerth, K. L.; Belina, K. M. Vineyard weed management practices influence nitrate leaching and nitrous oxide emissions. *Agric., Ecosyst., Environ.* **2010**, *38*, 127–131.
55. Kramer, S. B.; Reganold, J. P.; Glover, J. D.; Bohannan, B. J. M.; Mooney, H. A. Reduced nitrate leaching and enhanced denitrifier activity and efficiency in organically fertilized soils. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 4522–4527.
56. Yabaji, R.; et al. Nitrogen Management for Subsurface Drip Irrigated Cotton: Ammonium Thiosulfate, Timing, and Canopy Reflectance. *Soil Sci. Soc. Am. J.* **2009**, *10*, 345–354.

57. Camp, C. R.; Lamm, F. R.; Evans, R. G.; Phene, C. J. Subsurface drip irrigation: past, present and future. In *Proceedings of the fourth decennial irrigation symposium*, November 14-16, Phoenix, Arizona. American Society of Agricultural Engineers: St Joseph, MI; pp 363−372
58. Goldhamer, D. A.; Fereres, E.; Salinas, M. Can almond trees directly dictate their irrigation needs? *Calif. Agric.* **2003**, *57* (4), 138–144.
59. Khalil, M. A. K; Butenhoff, C. L.; Rasmussen, R. A. Atmospheric methane: trends and cycles of sources and sinks. *Environ. Sci. Tech.* **2007**, *41*, 2131–2137.
60. Feigin, A. Celery response to type, amount and method of N-fertilizer application under drip irrigation. *Agron. J.* **1982**, *74*, 971–977.
61. Haynes, R. J. Movement and transformations of fertigated nitrogen below trickle emitters and their effects on pH in the wetted soil volume. *Nutr. Cycling Agroecosyst.* **1990**, *23* (2), 105–112.
62. Bacon, P. E.; Davey, B. G. Nutrient availability under trickle irrigation: II. Mineral nitrogen. *Soil Sci. Soc. Am. J.* **1982**, *46*, 987–993.
63. Venterea, R. T.; Strock, J.; Rosen, C. Agricultural management effects on nitrous oxide gas emissions. In *Proceedings of the Lamberton and Outreach Center Soil and Water Management Field Day*, Lamberton, MN, 2008.
64. Kaiser, E. A.; Kohrs, K.; Kucke, M.; Schnug, E.; Munch, J. C.; Heinemeyer, O. Nitrous oxide release from arable soil: importance of perennial forage crops. *Biol. Fertil. Soils* **1998**, *28*, 36–43.
65. Millar, N.; Baggs, E. M. Chemical composition and or quality, of agroforestry residues influences N_2O emissions after their addition to soil. *Soil Biol. Biochem.* **2004**, *36* (6), 935–943.
66. Baggs, E. M.; Rees, R. M.; Smith, K. A.; Vinten, A. J. A. Nitrous oxide emission from soils after incorporating crop residues. *Soil Use Manage.* **2000**, *16*, 82–87.
67. De Neve, S.; Hofman, G. N mineralization and nitrate leaching from vegetable crop residues under field conditions: a model evaluation. *Soil Biol. Biochem.* **1998**, *30* (14), 2067–2075.
68. Novoa, S. A.; Tejeda, H. R. Evaluation of the N_2O emissions from N in plant residues as affected by environmental and management factors. *Nutr. Cycl. Agroecosyst.* **2006**, *75* (1–3), 29–46.
69. Glaser, B.; Lehmann, J.; Zech, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal –A review. *Biol. Fertil. Soils* **2002**, *35*, 219–230.
70. Lehmann, J.; Gaunt, J.; Rondon, M. Biochar sequestration in terrestrial ecosystem- a review. *Mitigation and Adaptation Strategies for Global Change* **2006**, *11*, 403–427.
71. Singh, B. P.; Hatton, B. J.; Singh, B.; Cowie, A. L.; Kathuria, A. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *J. Environ. Qual.* **2010**, *39*, 1–12.
72. Yanai, Y.; Toyota, K.; Okazaki, M. Effects of charcoal addition on N_2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. *Soil Sci. Plant Nutr.* **2007**, *53*, 181–188.

73. Rondon, M.; Molina, D.; Hurtado, M.; Ramirez, J.; Lehmann, J.; Major, J.; Amezquita, E. Enhancing the productivity of crops and grasses while reducing greenhouse gas emissions through bio-char amendments to unfertile tropical soils. In *Proceedings of the 18th World Congress of Soil Science*, Philadelphia, PA. 2006; pp 138–168 (IUSS/SSSA).
74. Sikora, L. J.; Szmidt, R. A. K. Nitrogen sources, mineralization, and nitrogen nutrition benefits to plants from composts. In *Compost utilization in horticultural cropping systems*; Stoffella, P. J., Kahn, B. A., Ed.; Lewis Publ.: Boca Raton, FL, 2001; pp 287–305.
75. Weier, K. L.; Doran, J. W.; Power, J. F.; Walter, D. T. Denitrification and dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate. *Soil Sci. Soc. Am. J.* **1993**, *57*, 55–73.
76. Steiner, C.; Das, K. C.; Melear, N.; Lakely, D. Reducing nitrogen loss during poultry litter composting using biochar. *J. Environ. Qual.* **2010**, *337*.
77. Van Zwieten, L.; Singh, B.; Joseph, S.; Kimber, S.; Cowie, A.; Chan, Y. Biochar reduces emissions of non-CO_2 GHG from soil. In *Biochar for environmental management*; Lehmann, J., Joseph, S., Eds.; Earthscan Publications Ltd: Oxford, U.K., 2010, pp 227–249.
78. Bouwman, A. F. Direct emission of nitrous oxide from agricultural soils. *Nutr. Cycl. Agroecosys.* **1996**, *46*, 53–70.
79. Parkin, T. B. Effect of Sampling Frequency on Estimates of Cumulative N_2O Emissions. *J. Environ. Qual.* **2008**, *37*, 1390–1395.
80. Brumme, D.; Beese, F. Effects of liming and nitrogen fertilisation on emissions of CO_2 and N_2O from temperate forest. *J. Geophys. Res.* **1992**, *97*, 12851–12858.
81. Fowler, D.; Skiba, U.; Hargreaves, K. J. Emissions of nitrous oxide from grasslands. In *Gaseous Nitrogen Emissions from Grasslands*; Jarvis, S. C., Pain, B. F., Eds.; CAB International: Oxon., U.K., 1997; pp. 147−164.
82. de Klein, C. A. M.; Sherlock, R. R.; Cameron, K. C.; van der Weerden, T. J. Nitrous oxide emissions from agricultural soils in New Zealand – a review of current knowledge and directions for future research. *J. R. Soc. N. Z.* **2001**, *31*, 543–574.
83. Barton, L.; Kiese, R.; Gatter, D.; Butterbach-Bahl, K.; Buck, R.; Hinz, C. Nitrous oxide emissions from a cropped soil in a semi-arid climate. *Global Change Biol.* **2008**, *14* (1), 177–192.
84. Barton, L.; Butterbach-Bahl, K.; Kiese, R. Nitrous oxide fluxes from a grain–legume crop (narrow-leafed lupin) grown in a semiarid climate. *Global Change Biol.* **2011**, *17* (2), 1153–1166.
85. Winiwarter, W.; Rypdal, K. Assessing the uncertainty associated, with national greenhouse gas emission inventories: a case study for Austria. *Atmos. Environ.* **2001**, *35* (32), 5425–5440.
86. Stehfest, E.; Bouwman, L. N_2O and NO emission from agricultural fields and soils under natural vegetation: summarizing available measurement data and modeling of global annual emissions. *Nutr. Cycling Agroecosyst.* **2006**, *74*, 207–228.

87. IPCC. Guidelines for National Greenhouse Gas Inventories. Volume 4: Agriculture, Forestry and Other Land Use. IPCC, Geneva, Switzerland, 2006.
88. Pattey, E.; Edwards, G. C.; Desjardins, R. L.; Pennock, D. J.; Smith, W.; Grant, B.; MacPherson, J. I. Tools for quantifying N_2O emissions from agroecosystems. *Agric. Forest Meteorol.* **2007**, *142* (2-4), 103–119.
89. Akiyama, H.; Yan, X.; Yagi, K. Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N_2O and NO emissions from agricultural soils: meta-analysis. *Global Change Biol.* **2010**, *16*, 1837–1846.
90. Halvorson, A. D.; Del Grosso, S. J.; Alluvione, F. Nitrogen Source Effects on Nitrous Oxide Emissions from Irrigated No-Till Corn. *J. Environ. Qual.* **2010**, *39* (5), 1554–156.
91. Halvorson, A. D.; Del Grosso, S. J.; Alluvione, F. Tillage and inorganic nitrogen source effects on nitrous oxide emissions from irrigated cropping systems. *Soil Sci. Soc. Am. J.* **2010**, *74*, 436–445.
92. Follet, R. F.; Shafer, S. R.; Jawson, M. D.; Franzulebbers, A. J. Research and implementation needs to mitigate greenhouse gas emissions from agriculture in the USA. *Soil Tillage Res.* **2005**, *83* (1), 159–166.
93. Rolston, D. E.; Sharpley, A. N.; Toy, D. W.; Broadbent, F. E. Field measurement of denitrification: 3. Rates during irrigation cycles. *Soil. Sci. Soc. Am. J.* **1982**, *46*, 289–296.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Chapter 13

N_2O Emissions and Water Management in California Perennial Crops

David R. Smart,[*,1] M. Mar Alsina,[1] Michael W. Wolff,[1] Michael G. Matiasek,[2] Daniel L. Schellenberg,[1] John P. Edstrom,[3] Patrick H. Brown,[4] and Kate M. Scow[2]

**[1]Department of Viticulture and Enology,
University of California, Robert Mondavi Institute North,
595 Hilgard Lane, Davis, CA 95616
[2]Department of Land, Air and Water Resources,
University of California, Plant and Environmental Sciences Building,
One Shields Avenue, Davis, CA 95616
[3]Cooperative Extension Colusa County, University of California,
P.O. Box 180, 100 Sunrise Blvd. Suite E, Colusa, CA 95932
[4]Department of Plant Sciences, University of California,
3041 Wickson Hall, MS-2, Davis, CA 95616
[*]E-mail: drsmart@ucdavis.edu. Phone: 530-754-7143. Fax: 530-752-0382.**

Greenhouse gas emissions from agriculture and forestry in California are estimated at approximately 8.3% of the total production of 493 million metric CO_2-equivalent tons (California Energy Comission (CEC); Research Roadmaps for Greenhouse Gas Inventory Methods; Sacramento, CA, 2005), of which nitrogen (N) fertilizers applied to soils and soil management are estimated to be the major sources of N_2O production. Of the approximate 3.89 million hectares (ha) of intensively irrigated cropland in California (California Department of Water Resources (DWR); Agricultural Water Use; Sacramento, CA, URL http://www.water.ca.gov/wateruseefficiency/agricultural/), approximately 1.17 million ha are planted to orchards and vineyards. This acreage is irrigated and fertilized with N using microirrigation systems and liquid N fertilizers (fertigation). Understanding biophysical factors that regulate N_2O emissions during fertigation will be necessary for scaling exercises, and

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

for developing sustainable management practices. We present ongoing work showing spatial variation in microbial enzyme activity in the microirrigation wet-up zone related to N_2O emissions and indicating that denitrifying microorganisms may be more abundant in the drip zone. Spatiotemporal variation in N_2O emissions around conventional aboveground drip and stationary fanjet micro-sprinkler systems in grape, a non-N-intensive perennial crop, and almond, a N-intensive perennial crop were well characterized using 3-dimensional modeling exercises. The quantity of N_2O emitted was lower when N was applied through stationary fanjet sprinklers than it was for conventional drip application in an almond orchard on a sandy loam soil.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Introduction

Importance of Agricultural N_2O Emissions and Perennial Crops

The increase in concentration of the three major greenhouse gases (GHGs) of carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4), is leading to adverse changes in climate. During the past 250 years, CO_2 has increased by 31±4%, CH_4 by 151±4% and N_2O by 19±5% (*3*). Resulting climatic alterations that will adversely affect California agriculture include increased temperatures, shifts in seasonal precipitation patterns, more restricted water resources (lower snowpack), and increasing frequency and duration of extreme events, like heat waves that result in yield loss (*4–7*). The current concentration of the GHG N_2O, the primary subject of this discussion, was 319 ppb in 2005 (*3*) as compared to its pre-industrial concentration of about 270 ppb. Nitrous oxide has 298 times the global warming potential (GWP) of CO_2 based on radiative forcing characteristics and atmospheric lifetimes of the respective gas molecules (*8*). Although the rate of increase of N_2O in the atmosphere (at about 0.27% per year) is much slower than that of CO_2 (and CH_4), this slower rate is offset by its higher GWP. The primary global sink for N_2O involves photolytic reactions with excited oxygen [O(1D)] in the stratosphere to produce nitric oxide (NO) which consumes stratospheric ozone (*9*).

Greenhouse gas emissions from agriculture and forestry in California are estimated at approximately 8.3% of the total estimated production of 493 million metric CO_2-equivalent tons (*1*), or about 41 million metric tons. If forest carbon (C) sequestration were removed from that estimate, the contribution of agriculture would be proportionally greater (*10*). Estimated emissions of agricultural GHGs in California indicated they consist primarily of N_2O (50.2% of the total) and CH_4 (34.5%), with CO_2 comprising only about 15.2% (*1*). Agricultural land represents a potential sink for sequestration of CO_2 through photosynthetic assimilation and deposition of assimilated C into soils (*11*). To determine the net potential for GHG reduction by agriculture practice in California, annual monitoring and total GHG budgets (CO_2, N_2O and CH_4) under conventional and alternative farming systems will be necessary.

Nitrous oxide is the single most important GHG generated by agriculture practice in California. Agricultural emissions of CO_2 are small and primarily released from the combustion of fossil fuels during field practices such as operation of tractors for soil cultivation, pest control, harvest-related activities and soil respiration. In addition, irrigation water pumping and frost control measures (*10*), like the operation of wind machines, consume energy and contribute to direct and indirect emissions of CO_2. Agricultural residue burning is a further source of non-fossil fuel derived CO_2, and such emissions depend on practice and local air quality restrictions. The synthesis of mineral-N fertilizers produces CO_2 during the Haber-Bosch process, which generates ammonium (NH_4^+) from hydrogen and dinitrogen gas (N_2) at high temperatures and pressure. As for methane, animal husbandry and rice production are responsible for the vast majority of agricultural production in California (*1*), and it is generally believed that upland agriculture systems like orchards and vineyards do not produce or consume significant quantities of CH_4, but this lacks verification. Finally, for N_2O, N fertilizers applied to soils and soil management practices (e.g., tillage) are estimated to be the major sources of N_2O production in California at 47.8% of total agricultural GHG emissions (*10*), while the other 2.4% (50.2% total) comes from manure management and burning of crop residues.

It is evident that N_2O as a GHG and reactive N species is important to the overall trace gas budget of the State. The link between N fertilizer use and N_2O emissions is under increasing scrutiny by regulatory organizations, but our level of understanding the agricultural N cycle in relation to trace gas budgets in California is poor. Nitrogen use efficiency (NUE), here defined as the quantity of N applied as fertilizer minus that lost to offsite transport in reactive forms, as a percentage of the total N applied, is not well quantified. In California cropping systems more research is needed regarding several factors influencing N-mobilization and N_2O emissions, including quantity and source of N fertilizer, soil and air temperature, application methods and temporal and spatial aspects of N_2O production in soils. Where possible, mitigation measures should be encouraged, but our understanding of how management factors influence emissions in California agriculture is extremely limited.

The objective of this chapter is to present information concerning spatial and temporal patterns of N_2O emissions at the vineyard and orchard scale. We focus primarily on emissions associated with the use of microirrigation systems for irrigation and fertilization (fertigation) of grape and almonds. We discuss methods to scale event-related emissions during fertigation events to the vineyard and orchard level and touch upon challenges associated with spatially constraining emissions. We conclude with possible N_2O mitigation scenarios for growers using fertigation in perennial crops.

California Perennial Crops and Microirrigation Systems

Of the approximate 3.89 million hectares of the total irrigated cropland in California (*2*), approximately 30% or 1.17 million hectares are planted to orchards and vineyards. Of that amount, roughly 0.95 million hectres (81%) are devoted to grapes (342,000 ha), almonds (328,000 ha), citrus (110,000 ha), walnuts (105,000

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

ha) and pistachios (62,000 ha). These perennial crops can be classified in terms of their N fertilization requirements, with grapes being less N-intensive while other fruit and nut crops are more N-intensive. Over 90%, or well over 1.0 million hectares of California perennial crops farmland is irrigated and fertilized using microirrigation systems. Use of flood irrigation has greatly declined as water available to agriculture in California has become more restricted (*12*). The most common microirrigation systems for perennial crops consist of aboveground drip (conventional drip) and stationary microjet sprinklers.

There are a number of clear advantages to production practices and water conservation when microirrigation is used. Many wine grape growers employ deficit irrigation in order to enhance fruit quality, and growers of other perennial crops can limit water use to improve management efficiency (e.g. dry-down of nut crop orchard floors to allow for mechanical harvesting). Many growers employ estimations of crop evapotranspiration (ET_c) to increase efficiency of water use (*13*). Microirrigation systems greatly facilitate the use of deficit irrigation practices because water can be accurately metered. Fertigation through these systems may improve NUE, since it allows for delivery of water and N using spatial and seasonal targets, for example during periods of peak fine root proliferation.

In California, woody perennial tree and vine crops can be generally grouped as those that are less water-intensive, like wine grapes and some of the stone fruits, and more water-intensive, which encompases a number of other fruit and nut crops. A transition may be under way towards increasing use of microjet sprinkler systems for crops with intensive water demand, such as almond, at 900 to 1,200 mm per season. In contrast, grapes in the moist North and Central Coastal regions are irrigated more conservatively, at 100 to 300 mm per year, and much less than full ET_c is used to improve fruit quality. Over 90% of grapes grown in California use conventional drip, while a small percentage are grown with border irrigation, sprinklers or under dryland conditions. Dryland farming usually features special conditions like high total available water in soils and/or high water tables, which are easily accessible by the deep rooting behavior of grapes (*14*). In comparison to nut crops and wine grapes, table grapes require intermediate amounts of water at approximately 300 to 600 mm per year.

Of the three major greenhouse gases emitted from agricultural systems (CO_2, CH_4 and N_2O), microirrigation systems probably have the strongest influence on N_2O emissions. The influence of microirrigation on N_2O emissions will depend on the spatial distribution of trees and vines, as well as on the timing of delivery of fertilizer with water. California orchards typically contain 125 to 450 trees per hectare, while vineyards include roughly 1,000 to 3,000 vines per hectare, with from 1 to 4 drip emitters or sprinklers per vine/tree. The distribution of fertilizer N through drip fertigation greatly increases the area-specific concentration of N, compared to that seen in field crops and furrow-irrigated crops. For example, with one drip emitter per vine and an 2.4 m row by 1.8 m vine spacing, we estimate that a 17 kg N per hectare (kg N ha^{-1}) application of N to a vineyard using 40% ET_c would result in concentrations of N in soil within the actual drip wet-up zone comparable to an uniform application of roughly 535 kg N ha^{-1} (*15*). Similar conditions might be seen for side-dress applications of N used in tandem with furrow irrigation of row crops (*16*). It is not proven, but likely, that elevated concentrations of mineral-N in the drip zone foster heightened activity and population levels of N-transforming microorganisms, and thereby increase potential N_2O emissions. Nevertheless, microirrigation systems allow directed applications of N that can match periods of maximum fine root proliferation and therefore N uptake (*17*), or phenological demand for N by N-intensive crops. Therefore microirrigation may favor vine and tree roots in competition with microorganisms for mineral-N. Nonetheless, the spatial distribution of water and N delivered by microirrigation systems is complex, depending on emitter type, number of emitters, spatial distribution of emitters, water emission rate and local soil characteristics (*18*).

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Biogeochemical Factors Involved in N_2O Emissions at the Vineyard and Orchard Scale

Microbiological Processes Contributing to Soil N_2O Emissions

To understand N_2O emissions from agroecosystems during fertigation events, it is important to have an understanding of N_2O biogenesis. The primary biogenic source of N_2O is the soil microbial community, through the N transformations brought about by nitrification and denitrification (*19*). It is generally accepted that denitrification produces more N_2O than nitrification, while nitrification produces more nitric oxide (NO) (*20*). Nitrification is an aerobic process involving the oxidation of ammonia (NH_3) or ammonium (NH_4^+) to NO_2^- and then to NO_3^-. Oxidation of NH_4^+ is performed by ammonia oxidizing bacteria using the enzyme ammonia monooxygenase (AMO) to form hydroxylamine (NH_2OH). Denitrification is the reduction of nitrate (NO_3^-) to nitrite (NO_2^-) and then N_2O and dinitrogen gas (N_2) by coupling NO_3^-/NO_2^- reduction to electron transport phosphorylation under limited oxygen (O_2) conditions.

Denitrification is carried out by an extremely diverse community of facultative heterotrophic microorganisms. These microbes can be generally classified into functional groups based on whether or not complete reduction of NO_3^- occurs, thus returning N to an oxidation state of zero and producing N_2 gas. When denitrification fails to proceed all the way to N_2, the process is viewed as incomplete. The production of N_2O gas, with an oxidation state of -1, is a product of incomplete denitrification. Incomplete denitrifiers, such as *Agrobacterium tumerfaciens* (*21*), *Pseudomonas chlororaphis,* or *Pseudomonas aureofaciens* (*22*), lack the enzyme nitrous oxide reductase (NOS). Previous investigation indicated that complete denitrifiers can generate N_2O during dissimilatory reduction of NO_3^- (*23*) but it is unknown what the contribution of complete versus incomplete denitrifier activity is in relation to total soil N_2O production.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

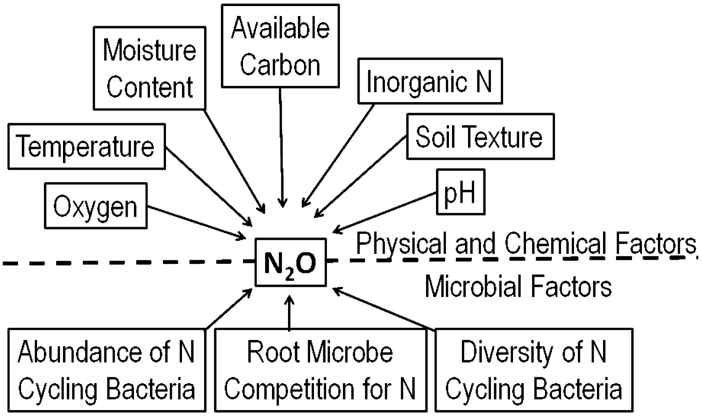

Moisture Content
Available Carbon
Inorganic N
Soil Texture
Temperature
pH
Oxygen
N₂O
Physical and Chemical Factors
Microbial Factors
Abundance of N Cycling Bacteria
Root Microbe Competition for N
Diversity of N Cycling Bacteria

Figure 1. The geochemical and microbiological variables hypothesized to influence N_2O production (24).

A number of physical and chemical variables influence N_2O production in California's Mediterranean climate and diverse soils (Figure 1). The most important at the landscape scale may be soil heterogeneity since it fosters the existence of diverse microbial communities, and conditions for N_2O production. Temperature is a key factor regulating activity of nitrifiers and denitrifiers (*25, 26*), with increasing rates observed up to 35°C (*27*), a temperature not uncommon in surface horizons of exposed California soils. Another major constraint on nitrification and denitrification is soil moisture, both as a limitation to biological activity when soils are dry, and because water-filled pore space (WFPS) influences aeration level. Water filled pore space is a measure of the proportion of soil pore space occupied by water. Particle size distribution determines WFPS for a given quantity of water delivered in a precipitation or irrigation event. Finer soils have more pore space than coarser soils but higher WFPS over time because small pore size results in more negative soil matric potentials (ψ_M) and therefore slower drainage.

Denitrification activity is generally heightened when WFPS exceeds 60-65% and anaerobic conditions predominate (*28–36*). Nitrification, on the other hand is favored by more aerobic conditions (*37*). Still, the WFPS transition point from aerobically-driven emissions to anaerobic emissions is not well understood (*38*). Most soils will have anaerobic microsites even under aerobic conditions. These apparent microsites exist within soil aggregates, where the diffusion of oxygen is limited (*39*). Under high WFPS, short-term limits on diffusion of trace gases (WFPS and solubility of gas in water) complicate observations of N_2O production (*40*) by following soil emissions, unless N_2O is sampled directly in the soil.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

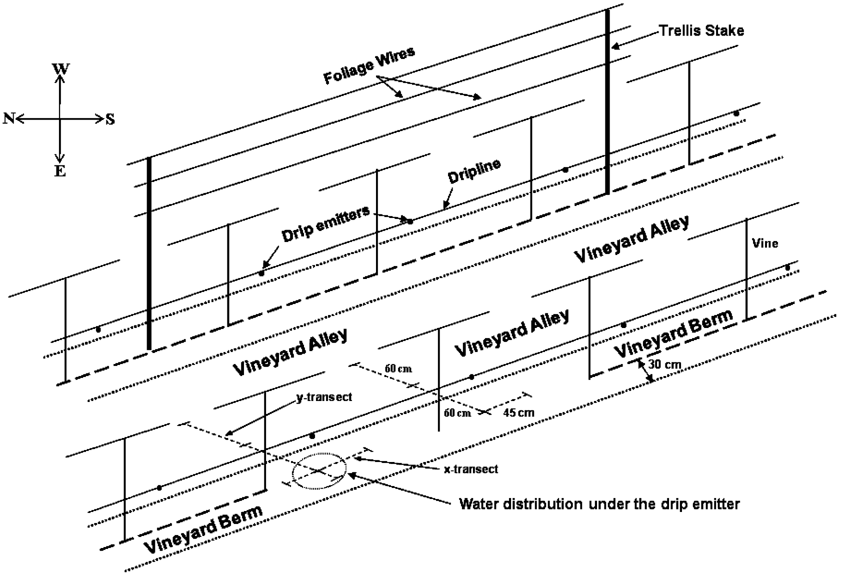

W
N
S
E
Foliage Wires
Trellis Stake
Dripline
Drip emitters
Vineyard Alley
Vine
Vineyard Alley
Vineyard Alley
Vineyard Berm
30 cm
60 cm
60 cm
45 cm
y-transect
x-transect
Water distribution under the drip emitter
Vineyard Berm

Figure 2. Spatial organization of vine row, berm, alley and drip emitters in a vineyard. The vertical T's represent vines which are trained onto a trellis system in bi-lateral cordons. Shown underneath the vines are the orientations of x and y transects used to describe microbial activity and N_2O gas flux. A surface distribution of soil moisture is shown, as delivered by drip irrigation emitters.

Spatial Variation in Microbial Activity Related to N_2O Emissions

Vineyards and orchards consist of rows of vines and trees with a managed area in between the rows, hereafter referred to as alleyways or alleys. The width of vineyard alleys ranges from 1.2 to 3.6 m, depending on variety and rootstock, tractor size and the goals of the individual operation. Trees in orchards have wider spacings, ranging from 4.8 to 12.1 m. The management of the row middle is diverse and depends on a number of factors including crop type, pest pressure, soil physical properties, slope and other site specific conditions that are beyond the scope of this review. The rows of trees/vines are sometimes managed with a raised (or non-raised) weed-free 'berm' of 0.3 to 1.2 m in width. This regular, imposed spatial pattern can have a strong influence on trace gas emissions, and adds another layer of complexity to the often heterogeneous distribution of bulk density, drainage, soil carbon and mineral-N and other physical and chemical properties of soils.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

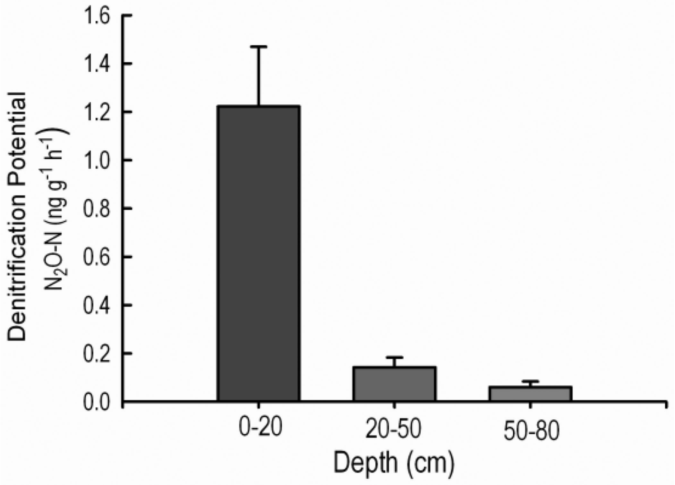


Figure 3. Soil denitrification potential from vineyard soils collected at depths of 0-20 cm, 20-50 cm and 50-80 cm. Samples were collected from within the drip irrigation zone (-20 to +20 cm, see Figure 5).

To gain a greater understanding of spatial patterns of microbial processes involved in N_2O production, we examined nitrification and denitrification enzyme activities in a vineyard in the Napa Valley of California that was conventionally managed for 12 years (38° 25’ N 122° 24’ W, at the University of California’s Oakville Research Station). The vineyard was irrigated twice a week with an estimated crop ETc of 40% or about 20 mm a week fertigated with KNO_3 at 17 kg N ha^{-1} y^{-1}. The soil is classified as a Bale loam (Fine-loamy, mixed, thermic Cumulic Ultic Haploxeroll). General soil textural characteristics (0–20 cm) were 25% clay 33% sand, 42% silt, saturated paste soil pH of 5.6 and bulk density of 1.22 ± 0.023 g cm^{-3} (Steenwerth et al, 2009).

Denitrifier enzyme activity (Figure 3) was limited to the Ap horizon at 0-20 cm depth. The alley in this vineyard was cultivated to 30 cm depth in late Spring and early Summer using two passes of a 1.2 m wide tandem disk. An undisked area of 30 cm on either side of the row (berm) was kept free of weeds with glyphosate applications (see Figure 2). Resident vegetation consisting of winter annual weeds was allowed to grow in the alleys and produced significant biomass under local conditions (*41*). We quantified denitrifier enzyme activity using the standard acetylene block assay (*42*) and nitrifier enzyme activity using the shaken slurry method of Hart and coworkers (*43*). We found the spatial distribution of nitrifier and denitrifier activity at this depth (20 cm) reflected water management. Nitrifier enzyme activity was heightened ($P < 0.05$) in soils in the alleys (2.30 ± 0.35 mg NH_4^+-N kg^{-1} soil day^{-1}, mean ± SE, n = 6) compared with the drip zone (1.17 ± 0.15 mg NH_4^+-N kg^{-1} soil day^{-1}). On the other hand, denitrification enzyme activity was slightly elevated ($P < 0.05$) in the drip zone (0.76 ± 0.05 μg N_2O-N g^{-1} h^{-1}) compared with the alley (0.56 ± 0.09 μg N_2O-N g^{-1} h^{-1}).

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

The C:N ratio of organic matter, and management practices that impact organic matter decomposition in soils, affect rates of N_2O emission (*44*, *45*). Soils with higher soil organic carbon (SOC) contents generally have higher N_2O fluxes, although results may be skewed by observations from marshland or estuarine soils with very high C contents (> 20%). In marshland soils, N_2O emissions are high due to predominantly anaerobic conditions rather than SOC *per se*. Nitrous oxide emissions do increase with additions of organic matter to soils (*32*, *46–49*), and the ratio of N_2O emitted to N applied can increase with SOC increase (*46*, *50*, *51*). Højberg and colleagues showed that N_2O emission 'hot-spots' in soils were correlated with carbon availability (*39*). These observations suggest that the observed increase in N_2O emissions with SOC is due to limitations of microbial activity by ratios and forms of C and N (*52*).

Spatial variation in N_2O flux has been found to be positively related to spatial heterogeneity in SOC content (*53–55*). We found soil C to be depleted in the drip zone in an analysis of the spatial distribution of soil C from the Oakville Research Station vineyard. The concentration of soil C outside of a radius of 20 cm of the drip zone center (*cf* Figure 2) was, on average, 913.4 ± 49.5 mg C kg^{-1} soil (mean ± SE, n = 9) and was approximately 9% higher ($P \leq 0.05$) than the C concentration within the drip zone (< 20 cm) at 835.7 ± 28.8 mg C kg^{-1} soil. Soil C to N ratios (C:N) were not significantly different within or outside the central area of the drip zone, at C:N = 12.03 ± 0.63 within a radius of 20 cm of the drip zone center and 12.14 ± 0.63 at > 20 cm from the drip zone center. Clearly, a lowering of soil C concentration within the drip zone corresponded with a lowering of N and does not offer a reasonable explanation for elevated denitrification enzyme potential, since carbon is known to stimulate denitrification activity, and observed C:N ratios were unfavorable to heightened microbial activity (*52*).

It is more likely that short-term changes in soil water content during irrigation, and availability of nitrate (NO_3^-) and ammonium (NH_4^+) during fertigation, explain the observed spatial distribution of nitrification and denitrification enzyme activity. Cultivation disturbance, since it increases aeration, decomposition and N mobilization, may explain why nitrification activity was heightened in the disked alleys. Water has the strongest influence on denitrification activity and N_2O emissions from soils because it affects the availability of oxygen. In soils, pore space is limited (< 50% total volume), and dissolved oxygen in water filled pore space is low. The saturation concentration for dissolved oxygen at standard temperature and air pressure is approximately 9 mg O_2 per liter, and this is consumed extremely rapidly in soils by respiration of roots and microbial organisms. Denitrification is a facultative process (*19*): denitrifying organisms can switch quickly between aerobic and anaerobic metabolism. Thus, saturation of soil pore space with irrigation water causes the onset of anaerobic conditions and fosters N_2O production. During the previous two decades, researchers working on soil N_2O production were able to establish strong relationships between soil texture, structure and WFPS for this reason (*45*, *56–60*).

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

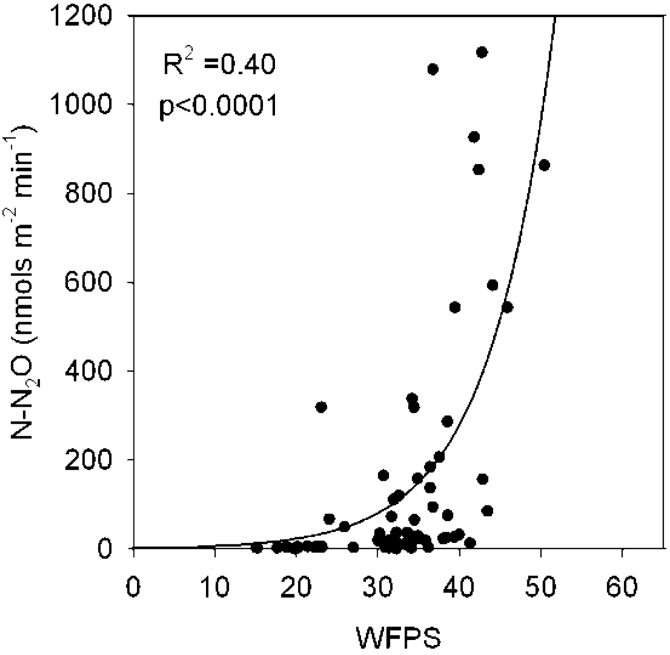


Figure 4. Nitrous oxide emissions as affected by water-filled pore space and N_2O emissions. (Nickels Soil Laboratory, 2009-2010).

For this discussion, it is important to understand the dynamics of soil water saturation and drying and how they influence WFPS during irrigation and fertigation events. Linkage of such dynamics to N_2O emissions will greatly facilitate modeling efforts to understand how management of California soils affects N_2O emissions. Although denitrification activity is reported to be heightened when WFPS exceeds 60-65% and anaerobic conditions prevail, we found the breakpoint between WFPS and N_2O emission following fertigation under field conditions to be somewhat lower. A significant relationship between WFPS and N_2O emissions (Figure 4) suggested the breakpoint where denitrification and therefore N_2O emissions increases was at approximately 40 to 50%. Mineral-N (soil NH_4+ and NO_3-) did not show a clear relationship with N_2O emissions rates (data not shown). These data were taken under field conditions, and thus N_2O solubility and other diffusion limitations when WFPS was high may have played a role. In other words, N_2O being produced under more saturated conditions might not be observed to be emitted from soils until pore space is sufficient for diffusion and N_2O released from solution (*30*). Nonetheless, the data indicated that any event that increases WFPS during irrigation or fertigation will increase emissions of N_2O.

Landscape Scale Variation Contributing to Soil N_2O Emissions

Fertigation simultaneously influences WFPS and the availability of substrates like mineral-N and dissolved organic carbon (DOC) that can limit overall

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

microbial activity. Temperature and moisture best explained emissions of the GHG CO_2 from conventionally tilled and no-tilled vineyards (*41*). In addition to these climatic and edaphic variables, other factors related to management practice are known to be quantitatively important to constraining N_2O budgets (*47*, *61–67*). Efforts to assemble quantitative N_2O budgets for California perennial crops must account for imposed spatial variation in addition to the numerous physical and chemical factors that contribute to emissions patterns (Figures 1 and 2).

Early workers seeking to understand N_2O flux from soils established linkages between N_2O emissions and soil temperature, WFPS, mineral N concentration (NO_3^- and NH_4^+), soil pH and SOC content (*54*, *68–74*). At the field scale, California's soils are extremely heterogeneous, and vineyards and orchards are typically planted over multiple soil types. Some studies have demonstrated how soil physical properties in the field can influence N_2O production at the landscape scale. For example, soil structure, perched water tables and texture (*58*, *75*, *76*) can be major determinants of N_2O production at the landscape scale and can also be determinate within individual orchards and vineyards (M. Mar Alsina and D. Schellenberg unpublished data). Croplands are reported to emit less N_2O than grasslands during periods when N transformations are not provoked by N fertilizer applications or cultivation, (*61*, *65*, *66*, *77*, *78*), and differences are emerging among crop types depending on N demand.

Short-term changes in mineral-N concentration and WFPS that occur during irrigation and fertigation using microirrigation systems are likely to have a strong influence on N transformations, and therefore on N_2O emissions. According to the hole-in-the-pipe model of Firestone and Davidson (*26*, *79*), the rate of emissions of N_2O is related to the rate of substrate transformation through nitrification and denitrification. As discussed, certain microbial organisms or environmental factors (Figure 1) can result in incomplete reduction of NO_3^- and 'leakage' of N_2O during denitrification as well as N_2O release during NH_4^+ oxidation by nitrifiers. At least NO_3^- and/or NH_4^+ as substrates for denitrification and nitrification are elevated in soils during fertigation, and are often delivered with enough water to mobilize organic C sources and temporarily saturate soil pore space.

At the landscape scale, the existence of extreme variability in naturally-occurring N_2O emissions has long been recognized as a challenge to accurate estimates of N_2O emissions (*80*, *81*). Although spatially dependent variation has been documented, observed autocorrelations have been observed at separations that do not necessarily correspond to landscape scale changes, eg. 1-10 m lags, (*6*, *54*, *73*, *82*). Nevertheless, Turner and colleagues (*83*) describe autocorrelations at a larger scale for fields with very high N_2O emissions rates. This and other evidence (*84*) indicate that multiple spatial structures exist for N_2O emissions at the landscape level (*58*).

Multiple spatial scales for N_2O emissions make sense, considering that topographical features influence soil depth, bulk density, drainage patterns (*85*) and other factors that influence denitrification. The existence of 'hot spots' of denitrification activity is a well known phenomenon in soil microbial ecology and in microbial physiological research. A number of conditions probably contribute to the existence of 'hot spots', including high concentrations of carbon (*55*), low redox potential (*86*), diminished aeration status (*87*) as a consequence of

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

compaction or poor drainage, as well as population density and composition of microbial communities (M.G. Matiasek, unpublished data).

The existence of natural spatial variation in denitrification and nitrification activity, driven mainly by soil environmental factors, complicates the characterization of N_2O emissions in orchards and vineyards. Naturally occurring variation in these settings is overlain with regular patterns related to management practices. Attempts to characterize spatial variation for N_2O emissions in orchards and vineyards are extremely limited if not nonexistent. For furrow irrigated field crops, the basic model adopted for constraining and scaling chamber-based N_2O emissions measurements to the field level use a 'geometric' model (*16*). In other words, emissions measured at defined horizontal patterns across furrows and planting beds are assumed to be uniform along the row. Ball and colleagues found the assumption of uniform short-range (< 2 m) variation in N_2O emissions in winter barley (*Hordeum vulgare*) and oil-seed rape (*Brassica napus*) were not valid, nor did N_2O emissions correlate with soil chemical and physical factors for straw mulch versus areas with compacted soils (*88*). Thus, the assumption of uniformity along the row in many scaling exercises is probably unrealistic, yet it represents the most consistent method given the labor intensity of N_2O measurements. There is furthermore, a paucity of good micrometeorological measurement tools to ground-verify results obtained from the scaling of small static chamber measurements to the field level.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Spatiotemporal Variation in N_2O Emissions at the Vineyard Scale

Grids of small static gas flux chambers can be useful for describing spatial patterns of emissions at small scales. To characterize spatial variation in N_2O emissions around drip irrigation emitters, we laid out static chambers along x- and y-transects (Figure 2) in a drip-irrigated vineyard. The x-transect was taken parallel to the vine row and the y-axis was perpendicular to that, leading into the center of the alley, at positions of -25, -15, 0, +20, +40, +60, +80 and +120 centimeters from the center of the drip emitter at (0,0). The vineyard alleys were disked and rolled in Spring (April) when native, weedy vegetation reached anthesis. Fertigation took place in late June that season, at a rate of 17 kg N ha^{-1}. Observations within the alley were rotated 90° to provide no less than 7 observations for each transect direction. This approach is based upon the assumption that the distribution of N_2O emissions around each drip emitter is uniform. Subsequent evaluation using multiple chambers in both grape and almond systems on similar soils under drip irrigation demonstrated the assumption to be correct (M. Mar Alsina, unpublished data). Nitrous oxide emissions (nmol N_2O-N m^{-2} min^{-1}) from each of three repetitions of the 7 flux chambers, with 2 transects and three reps (n = 3), were fitted to Gaussian distributions (SYSSAT, version 11.0) according to:

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

$$f(N_2O)_x = z_0 + a \cdot e^{\left[\frac{(x-x_0)^2}{2b^2}\right]}$$

eqn. 1

$$f(N_2O)_y = z_0 + a \cdot e^{\left[\frac{(y-y_0)^2}{2c^2}\right]}$$

eqn. 2

where z_0 is the estimated baseline N_2O emission rate outside of the drip irrigation zone of influence, x and y are the x and y coordinate positions with respect to the soil impact zone of the drip emitter at coordinate (0, 0) and a is the maximum estimated emission rate at the center of the drip zone (see Figures 5 and 6). The N_2O emissions rates were then integrated over the plane defined by a line paralel to the vine row and another perpendicular to it, using a 5 cm grid, and at a distance of 0.5 m along either the x or the y axis. The grid was established with the coordinate (0, 0) as the rate of N_2O emissions (z) in the center of the 0.5 x 0.5 m grid, and the rate over the whole surface was calculated as a sum of that in each of the cells according to:

$$z = \sum_{x=-50}^{x=+50} \sum_{y=-50}^{y=+50} z_0 + a \cdot e^{\frac{1}{2}\left[\frac{(x-x_0)^2}{b^2} + \frac{(y-y_0)^2}{c^2}\right]}$$

eqn. 3

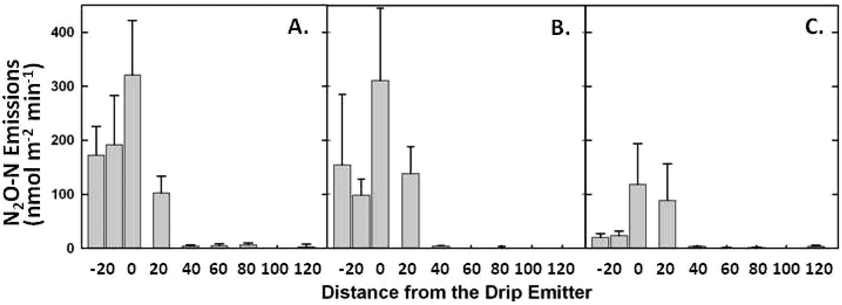


Figure 5. Spatial variation in nitrous oxide emissions along the x- and y-transects through the drip zone depicted in Figure 2. Shown are the means and standard errors of the means (n = 3), for the positions of -25, -15, 0, +20, +40, +60, +80 and +120 cm taken at 9:00 a.m. (A), 12:00 noon (B) and 3:00 p.m. (C).

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Spatial variation in soil N_2O emissions was extreme (Figure 5), with the coefficients of variation for each individual spatial transect coordinate ranging from 22.6% to 146.6%. For example, at 9:00 a.m. and 12 p.m., which were at 12 h and 15 h following fertigation, respectively, N_2O emission rates ranged from 121.6 to 569.7 nmols N_2O-N m^{-2} min^{-1} (n = 6) at the origin of the x and y transects (Figure 6). On the other hand, the spatial pattern of emissions during 24 h following fertigation was highly discernible (Figure 5). Of the eighteen transects evaluated, twelve produced statistically significant fits ($P < 0.05$) to a Gaussian distribution with coefficients of variation ranging from $R^2 = 0.549$ ($P = 0.2281$) to $R^2 = 0.958$ ($P = 0.0007$). Thirteen of the eighteen regressions produced fits of better than $R^2 = 0.80$ (Table I).

Table I. Statistical parameters for fits of drip zone N_2O emissions to Gaussian distributions. y_o is the baseline emission rate for areas outside the drip irrigation zone of influence while A is the maximum rate of emission at the center of the drip zone.

Time	*transect,*	*R^2*	*y_o (nmol N_2O-N m^{-2} min^{-1})*	*A (nmol N_2O-N m^{-2} min^{-1})*	*P > F*
a.m.	x-transect, R_1	0.801	-2.17 ± 4.89	245.1 ± 189.9	0.0305
a.m.	x-transect, R_2	0.826	8.39 ± 3.91	185.3 ± 63.6	0.0241
a.m.	x-transect, R_3	0.712	24.86 ± 11.47	433.1 ± 219.1	0.0802
a.m.	y-transect, R_1	0.893	-17.47 ± 3.96	262.7 ± 118.9	0.0074
a.m.	y-transect, R_2	0.844	2.99 ± 3.41	190.8 ± 62.8	0.0186
a.m.	y-transect, R_3	0.843	-8.57 ± 8.99	478.7 ± 240.9	0.0187
noon	x-transect, R_1	0.556	-4.46 ± 3.59	94.4 ± 121.5	0.2204
noon	x-transect, R_2	0.549	-17.18 ± 7.69	204.7 ± 285.7	0.2281
noon	x-transect, R_3	0.931	9.84 ± 6.29	579.0 ± 99.1	0.0024
noon	y-transect, R_1	0.888	-1.47 ± 4.26	132.8 ± 30.5	0.3750
noon	y-transect, R_2	0.714	22.65 ± 5.24	218.1 ± 58.18	0.0797
noon	y-transect, R_3	0.958	-8.22 ± 5.09	607.9 ± 76.9	0.0007

Continued on next page.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Table I. (Continued). Statistical parameters for fits of drip zone N_2O emissions to Gaussian distributions. y_o is the baseline emission rate for areas outside the drip irrigation zone of influence while A is the maximum rate of emission at the center of the drip zone.

Time	*transect,*	*R^2*	*y_o (nmol N_2O-N m^{-2} min^{-1})*	*A (nmol N_2O-N m^{-2} min^{-1})*	*P > F*
p.m.	x-transect, R_1	0.868	1.44 ± 4.00	32.09 ± 5.8	0.0124
p.m.	x-transect, R_2	0.916	-1.14 ± 3.47	286.3 ± 54.3	0.0041
p.m.	x-transect, R_3	0.951	6.47 ± 6.14	71.8 ± 7.0	0.0011
p.m.	y-transect, R_1	0.615	7.58 ± 4.10	26.4 ± 10.2	0.1594
p.m.	y-transect, R_2	0.985	8.82 ± 1.20	255.9 ± 13.53	<0.0001
p.m.	y-transect, R_3	0.992	2.77 ± 2.59	75.6 ± 2.99	<0.0001

Consensus distributions from the combined datasets of Table I produced fits exceeding $R^2 = 0.956$ and $P \leq 0.01$. These consensus fits were used to develop three-dimensional models of N_2O emissions in the drip zone using equations 1, 2 and 3 (Figure 6). These models provide N_2O emissions estimates that can be scaled to the field level. By knowing the number of emitters per hectare, which, in vineyards is generally two emitters per vine, a geometric approach can be employed to scale these emissions estimates to the vineyard level. There are some exceptions, where site specific conditions call for more or fewer emitters per vine, lower water emission rates, or additional microirrigation lines are established for replants. But in general these represent exceptions to the norm of two emitters per vine. The baseline rates outside of the emissions 'plumes' (see Figure 6) can then be used to estimate emissions outside of the 0.5 by 0.5 meter area of the drip zone. This scaling exercise differs from 'geometric' models that generally consist of single chambers placed over a row area (furrow, berm, planting bed), and scaled up based on the in-field proportional area of the measured row. These approaches are not valid for the estimation of emissions from microirrigation systems, which are point sources.

As seen above (Figure 6), we were able to constrain N_2O emissions during a fertigation event involving approximately 38 liters KNO_3 solution per vine, using a simple Gaussian distribution. However, it is not uncommon for practitioners to 'chase' fertigation solutions with N-free irrigation water. We have found this alters the spatial pattern of N_2O emissions, apparently because lateral (axial) movement of mineral N through mass flow and diffusion. This resulted in a more complex pattern of water and mineral-N distribution and, as a consequence, a non-uniform and more complex pattern of N_2O emissions (Figure 7). In this case, transects again were established both across and parallel to the vine row (Figure 2) and N_2O emissions were directly measured at -25, -15, 0, +20, +40, +60, +80, and

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

+120 cm from the origin, which corresponded to the drip impact zone. Since a simple Gaussian distribution did not well explain the pattern of N_2O emissions observed, alternative functions and relationships remain to be investigated for these distributions.

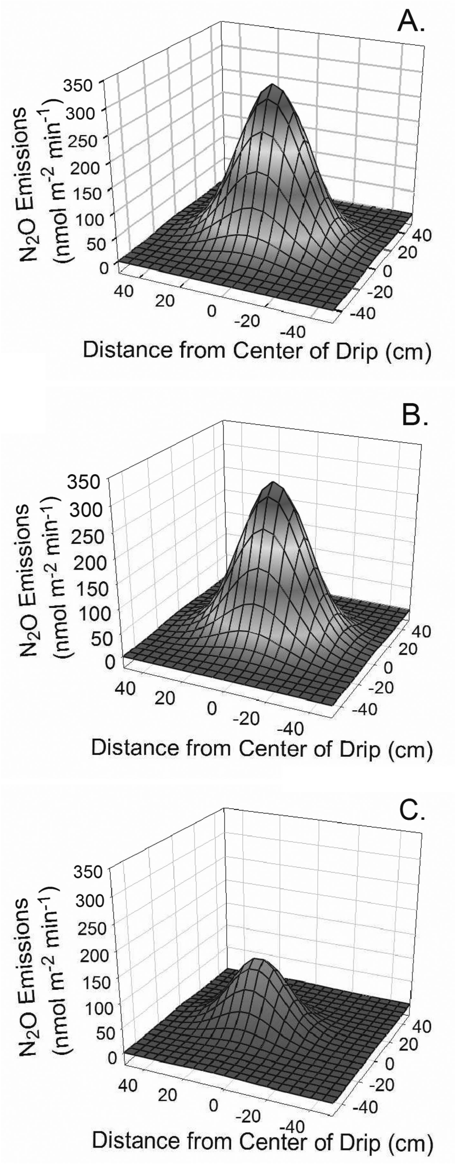


Figure 6. Shown are modeled emissions for a 17 kg N per ha fertigation event in a vineyard. Transects were established both across and parallel to the vine row where N_2O emissions were directly measured. Shown are models of Gaussian distributions of emissions for 9:00 a.m. (A.) 12:00 p.m. (B.) and 3:00 p.m. (C.) following an overnight fertirrigation event.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

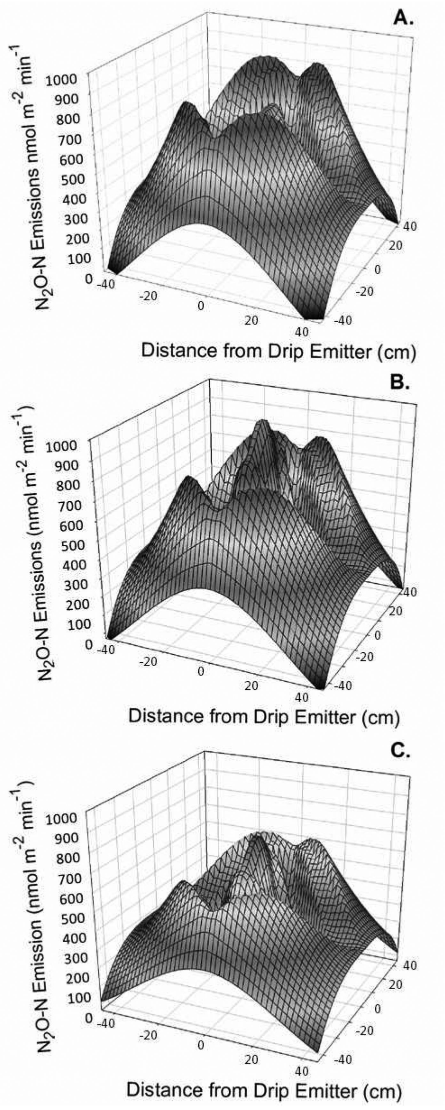


Figure 7. Shown are modeled N_2O emissions following a drip fertigation event of 8.5 kg N ha^{-1} as $Ca(NO_3)_2$. The solution was applied as 6 liters of solution delivered per emitter per vine and was followed by 21 liters of irrigation water. The emissions data to develop the 3-dimensional models shown were taken at 1 hour (A.), 3 hours (B.) and 6 hours (C.) following the end of the fertigation/irrigation event.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Spatiotemporal Variation in N_2O Emissions at the Orchard Scale

Almond, citrus and other orchards in general are more N and water intensive than vineyards, so orchards can have from four to eight drip emitters per tree, or employ microjet sprinkler systems. It is important to establish spatial patterns of N_2O emissions in orchards, and to assess whether total N_2O emitted per hectare of an orchard might be substantially influenced by the microirrigation system used (microjet sprinkler versus drip). To achieve this objective, N_2O emissions were monitored after fertigation events and over time, again using a series of transects in an orchard experiment employing treatments of stationary microsprinkler versus conventional drip (Figure 8). We selected almond because, unlike grape, it is a more N intensive crop. Growers throughout California use a mixture of drip and microjet sprinkler systems, and little data is available concerning either orchard performance or N trace gas emissions under the two microirrigation approaches.

The measurements were carried out at the University of California's Nickels Soil Laboratory, in Arbuckle, CA (39°01′ N 122°03′ W) using an experimental almond orchard with a completely randomized block design for microirrigation systems (*89*). The yearly water and fertilizer supply was the same for each treatment, and was applied no more than one day apart for each treatment. The orchard was planted with a nonpareil cultivar and the trees were on an 4.85-m in-row by 6.75-m between-row spacing. Irrigation amounts were regulated at approximately 40% of the estimated crop evapotranspiration demand (ET_c) as estimated from the Penmann-Monteith relationship, evaporation from a Class A pan and adjusted using an almond crop coefficient (K_c). Two different microirrigation systems were compared: single hose drip irrigation, consisting of 4, 3.8-liter-per-hour (lph) emitters per tree, and microjet sprinkler (at 15,2 lph), with one sprinkler head per tree. Total hours of irrigation were calculated to deliver the same amount of water in both treatments during each fertigation event.

In order to better quantify soil N_2O emissions generated around emitters during fertigation events, we designated a circular area of 1 m in diameter for drippers and of 5 m diameter for the microjet sprinklers. We refer to this as the 'wet-up area'. We established two transects of static chambers, forming axes crossing at the drip irrigation emitter impact point or sprinkler nozzle, which was designated as the origin (0, 0). Transects were established under three different trees in each of the two irrigation systems (in three separate experimental blocks, n=3). One transect (N-S, y-ordinate) was established parallel to and within the tree row, and the other (E-W, x-ordinate) perpendicular to the tree row, leading out into the alley (see Figure 8). In each of these transects we determined 5 positions where soil N_2O flux was sampled. Thus 10 positions per site were used to determine the N_2O emission distribution around the microjet sprinkler or drip emitter.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

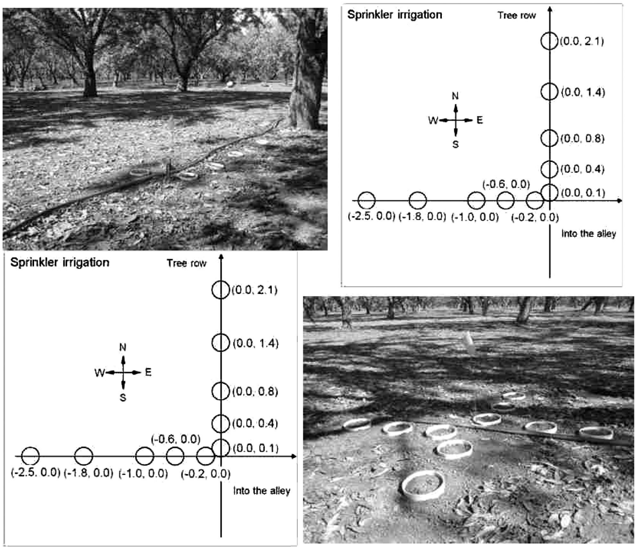


Figure 8. Distribution of collars for gas flux chambers to measure N_2O emissions for conventional drip irrigation (above) and fanjet sprinkler (below).

Drip irrigation showed a peak of emissions in the center followed by a rapid decline as the distance from the emitter increased, reaching values close to zero at distances of about 1 meter from the center (Figure 9). This was very similar to what we observed for N_2O emissions under drip emitters in vineyards (Figure 6). In contrast to drip, distribution of N_2O emissions under microjet sprinklers showed the peak of emissions at a distance around 1 meter from the sprinkler head, which then decreased exponentially until values close to zero were reached at distances of 2.5 – 3 meters from the emitter (Figure 10). We generally refer to this as a ‘doughnut’ pattern of emission. Our findings indicated N_2O emissions patterns were similar to known water distribution patterns for the microjet sprinkler and drip irrigation systems. Emissions were again well constrained with fits to a Gaussian distribution for conventional drip, with R^2 values that exceeded 0.90. This observation suggests that it might be feasible to model and estimate N_2O emissions using models of water distribution patterns (Figures 6 and 7). Soil moisture in perennial crops irrigation systems in Mediterranean climates is a primary environmental variable in driving GHG emissions (*41*, *90*), but we are finding the temporal patterns of emissions differ. These complexity of constraining emissions from localized fertigation events over time (9 to 14 days, Figure 10 *cf* Figure 6). This may relate to the fact that drip irrigation patterns of water distribution are not always uniform (*91*), and depend on soil texture, depth, compaction and other physical variables.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

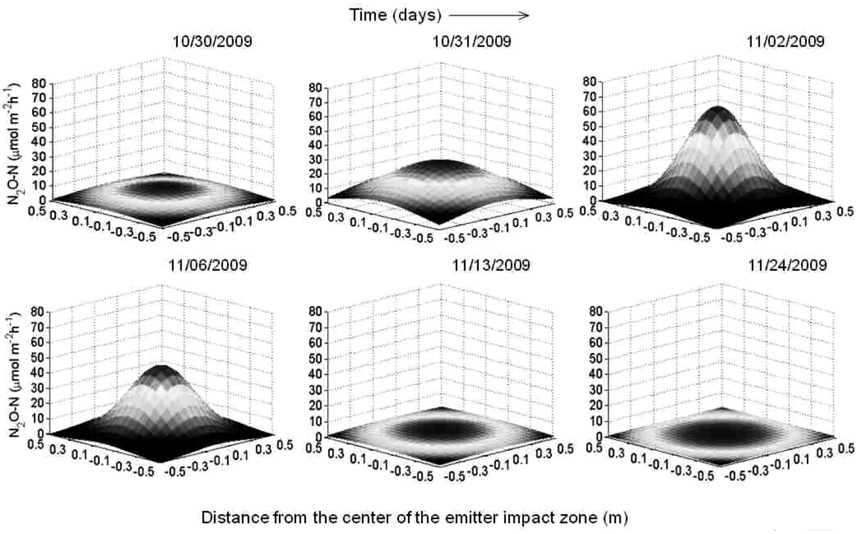


Figure 9. Distribution of N_2O emissions under a drip emitter following a fertigation event of 34 kg N ha^{-1} in an almond orchard. The distributions of emissions shown were derived from three-dimensional fits of the Gaussian distribution.

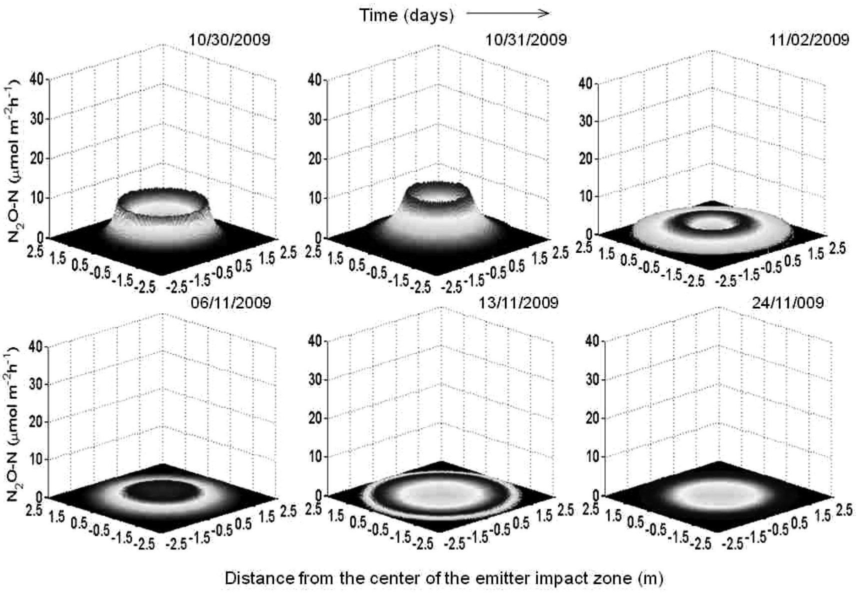


Figure 10. N_2O emissions distributions from microjet sprinkler delivered fertigation. The 3-dimensional models were derived from fits of functions defined by two parts: a second degree polynomial and an exponential decay.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Having derived functions that best define patterns of N_2O emission from the wet-up area around the water emitter, these instantaneous rates of N_2O-N emission can be integrated over the course of time of the fertigation event. The ‘event’ timeline can be considered as the length of time passing before emissions return to baseline values. Here the N_2O emissions event duration was at least two weeks (Figures 9 and 10). We monitored N_2O using the described spatial methods during 15 days after two fertigation events consisting of calcium ammonium nitrate (CAN) at 34 kg N ha^{-1} in the Fall of 2009 and Spring of 2010, when air (Figure 11) and soil temperatures (data not shown) were similar. The maximum rates of N_2O emission corresponded to levels of 944 nmol N_2O-N m^{-2} min^{-1} and 300 nmol N_2O-N m^{-2} min^{-1} for drip and sprinkler irrigation respectively in Fall 2009. They were 1,165 nmol N_2O-N m^{-2} min^{-1} and 219 nmol N_2O-N m^{-2} min^{-1} for drip and sprinkler in Spring of 2010. These represent instantaneous rates at point sources in the wet-up area, not yet scaled to the level of the entire wet-up area and time period of the emission event. As previously discussed, the areas wetted by the sprinkler and drip systems only represent a fraction of the total area of the orchard. For this reason, the total quantities of N_2O-N loss won’t be accurate until the ‘non-wet-up area’ is included in the exercise. To calculate the non-wet-up area emissions, the geometric model was followed, considering the emission to be constant over the entire area of the vineyard/orchard that was not within the zone of irrigation influence. Thus, our scaling exercise uses the geometric approach but includes the variability in N_2O emissions within the emitter wet-up zone. Clearly, emissions of N_2O from a fertigated orchard or vineyard would be over-estimated if the approach were geometric alone, but we are uncertain to what degree accuracy is increased.

Nonetheless, the emission rates indicated that total loss of N as N_2O was still higher from the drip than from microjet sprinkler irrigation. During the Fall fertigation event, microjet sprinklers showed a peak of N_2O emissions one day after fertigation and then a gradual decline until emissions reached baseline values about 2 weeks later (Figure 10 and 11). Under drip the dynamic was slower: Peak emissions were seen on day 3 (Figures 9 and 11), and emissions remained slightly elevated 2 weeks later. After delivering an equivalent amount of solution in a single fertigation event to drip and microjet sprinkler, soils under drip irrigation appeared to remain saturated longer in the central area of water distribution. We therefore speculate the 50% level of WFPS (Figure 7) is exceeded for a longer duration in drip wet-up areas than in microjet sprinkler wet-up areas. Water was distributed over a larger area by the microjet sprinklers. Because the area specific quantity of water applied is lower, soils may drain relatively faster than drip irrigation and maximum soil water contents may not exceed the critical level for N_2O emissions to increase (Figure 3). Soil drying was also faster in the microjet sprinkler wet-up area. The combination of these two factors may explain why we saw lower peaks and lower total emissions in microjet sprinkler wet-up areas.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

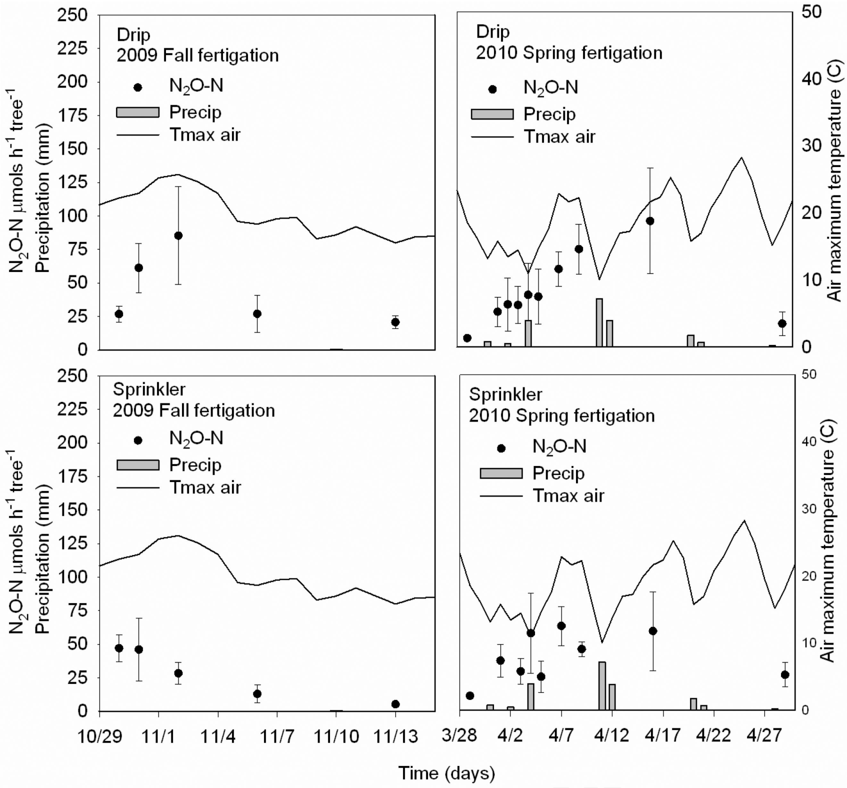


Figure 11. Shown are the integrated N_2O emissions on a per tree basis for Fall (left panel) and Spring (right panel). Fertigation events of 34 kg N ha^{-1} were applied using either drip or microjet sprinkler delivery systems. Each data point represents the instantaneous emissions integrated over the wet-up area corresponding to a tree and were obtained by integration of the 3-dimensional models shown in Figures 9 and 10.

In Spring, the N_2O emissions patterns were much more complex (Figure 11). Nitrous oxide emissions did not show a discernible peak moment in either the drip or the microjet sprinkler fertigated systems. Rather, emissions were highly erratic and driven by 7 individual precipitation events that occurred during a three-week period following fertigation. The dynamics of N_2O emissions during these consecutive precipitation events is complicated by the aforementioned biophysical influences of water on N_2O, including the gas's high solubility in liquid water (*92*). For example, following an emissions peak during the precipitation event of April 4, 2010 in the sprinkler irrigated treatment (Figure 11, lower right panel), emissions dropped back down to a very low level on the next day. In contrast, emissions remained high in the drip treatment (Figure 11, upper right panel) following that precipitation event. We note that before precipitation occurred, soil water content already differed by treatment. The drip zone was much closer to saturation than was the microjet sprinkler area, and may explain why rain affected microjet sprinkler emission patterns much more strongly.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

As pointed out earlier, a major impediment to accurate estimates of N_2O emissions from vineyards and orchards is the formulation of an approach to scale up chamber-based measurements to the vineyard or orchard level (hectares). To scale the values obtained in the wet-up area to the orchard, we divided the orchard into two areas. One was represented by the total wet-up area, obtained by scaling the wet area per drip emitter or per microjet sprinkler according to the total number of emitters/sprinkler heads in a hectare. In this area, the emission was calculated by integrating the small scale spatially derived functions described above. In the rest of the orchard area, the values of flux used to calculate the amount of N_2O-N per hectare per hour corresponded to the flux measured in the orchard alley 2.5 meters from sprinkler heads and 1.6 meters from drip emitters. These positions were considered to be minimally affected by the irrigation and/or fertigation events. The measured flux at these positions was considered to be representative of all the non-wetted area in the orchard. A ‘geometric’ model was used to calculate the total N_2O-N loss from the non-wet-up area.

The values of N_2O-N loss we measured per event per hectare were lower for microjet sprinkler fertigation than for drip (Table II). In both seasons and for both irrigation types, N_2O emissions were estimated to be less than 0.4% of the total N applied. This represented an application of 34 kg N ha^{-1}. During the Fall fertigation (Table II) only 83 g of N ha^{-1} under drip irrigation and 49 g of N ha^{-1} under sprinkler irrigation were lost in N_2O form, while in Spring the values were 191 g and 122 g, respectively. These values corresponded to 0.30% and 0.18% of total N applied in the Fall, and 0.70% and 0.45% for the Spring event, for drip and microjet sprinkler respectively. Thus, preliminary data at this site, which has a well drained soil, indicated that the use of microjet sprinklers instead of drip irrigation would reduce the N_2O-N loss by as much as half. It must be kept in mind that we do not know how much of the N is absorbed by trees and other vegetation, or assimilated into microbial biomass and retained in soils. Nonetheless, the 0.2% to 0.7% loss observed only represents the N lost during the event period.

Conclusions and Mitigation Potential

Grape and nut crops constitute the vast majority of perennial crops acreage in California. Here we present evidence showing that the major N_2O loss from these crops follows N fertigation. Water and liquid-N applications to these crops are accomplished mainly through the use of microirrigation and fertigation systems. These systems allow for precise metering of water and N, but add a layer of complexity over the already existing heterogeneity of of soil physical properties and environmental factors that control N_2O production and release. We conclude that placement of a single gas chamber over the impact point of a drip emitter, or in the wet-up area of a microjet sprinkler, will be insufficient to accurately gather event-related N_2O emissions data and scale it to the vineyard and orchard level. Events that alter N-mineralization rates, mineral-N mobilization and WFPS, such as irrigation, fertigation and precipitation, are of relatively high frequency in California perennial crops systems. Therefore, constraining such events on a spatiotemporal basis is critical to accurate reporting of N_2O budgets in perennial crops.

We found that N_2O emissions around microirrigation systems during fertigation events could be well characterized and better constrained using 3-dimensional models (see Figures 6, 7, 9 and 10). These models allow for better estimation of landscape scale emissions of N_2O in vineyards and orchards than do geometric models, which are more appropriate for row crop systems (*16*). They call into question previous estimates for N_2O emissions from vineyards and orchards at the landscape scale (*93*, *94*).

We have verified that constraining N_2O emissions will depend in large part upon factors like WFPS, substrate availability, and microbial activity for California soils and perennial crops farming practices. These practices include management of vegetation in row middles, tillage, irrigation and fertilization. Because the quantity of N_2O being emitted is not yet well understood, we are also beginning to examine the dependency of N_2O emissions on row management in California perennial crops. The adoption of no-till and other practices in the California agricultural landscape, which are intended to increase soil carbon sequestration (*11*, *95*), may have significant effects on N_2O emissions. For vineyards and orchards, the addition of manure, composts or other forms of organic matter represents another corresponding knowledge gap. Nonetheless, it is certain that management practice influencing disturbance (tillage), short-term conditions of WPFS (irrigation) and mineral-N concentration (fertigation) all affect microbial community activity and N_2O production. In each of these practices lie potential improvements which could at least partially mitigate N_2O emissions.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Table II. N_2O-N emissions (g N_2O-N ha^{-1}) during two fertigation events in Fall of 2009 and Spring of 2010. Each value comes from the numeric integration of the measured instantaneous emissions over space and time.

				N_2O Emission (g N_2O-N ha^{-1})	
Fertigation Event	*Starting Date*	*Ending Date*	*Days*	*Drip Irrigation*	*Microjet Irrigation*
Fall 2009	10/30/09	11/24/09	25	83	49
Spring 2010	3/29/10	4/29/10	31	191	122

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Acknowledgments

We acknowledge the Kearney Foundation of Soil Science under agreement number 2006-000 and 2009-029 to David R. Smart, Peter Hernes, Krassimira Hristova and Kate M. Scow; the Almond Board of California under agreement 2009-AIR2 to D. R. Smart; the American Vineyard Foundation under agreement 2009-818 to D. R. Smart; the United States Department of Agriculture under agreement 2009-34360-20160, awarded to D. R. Smart and Kate M. Scow. We thank Dr. Roger Boulton and Mrs. Megan Kyles for assistance with the statistical analyses, and we thank Dr. Kerri Steenwerth of the USDA ARS for assistance with collection of the grape field data.

References

1. California Energy Comission (CEC); *Research Roadmaps for Greenhouse Gas Inventory Methods*; Sacramento, CA, 2005.
2. California Department of Water Resources (DWR); *Agricultural Water Use*; Sacramento, CA, URL http://www.water.ca.gov/wateruseefficiency/agricultural/.
3. Forster, P.; Ramaswamy, V.; Artaxo, P.; Bertsen, T.; Betts, R.; Fajey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; Van Dorland, R. Changes in Atmospheric Constituents and in Radiative Forcing. In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007.
4. Prather, M. *Climate Change*; Cambridge University Press: New York, 1994; pp 73−126.
5. Hayhoe, K.; Cayan, D.; C.B., F.; Fumhoff, P. C.; Maurer, E. P.; Miller, N. L.; Moser, S. C.; Schneider, S. H.; Cahill, K. N.; Cleland, E. E.; Dale, L.; Drapek, R.; Hanemann, R. M.; Kalkstein, J. L.; Lunch, C. K.; Neilson, R. P.; Sheridan, S. C.; Verville, J. H. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 12422–12427.
6. Houghton, J. T.; Meiro Filho, L. G.; Callander, B. A.; Harris, N.; Kattenburg, A.; Maskell, K. *Climate change 1995: the science of climate change*; Cambridge University Press: Cambridge, U.K., 1996.
7. White, M. A.; Diffenbaugh, N. S.; Jones, G. V.; Pal, J. S.; Giorgi, F. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 11217–11222.
8. *IPCC, Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, 2001.
9. Cicerone, R. J. *Science* **1987**, *237*, 35–42.
10. Carlisle, E.; Smart, D.; Williams, L.; Summers, M. *California Vineyard Greenhouse Gas Emissions: Assessment of the Available Literature and Determination of Research Needs*; San Francisco, CA, 2010.

11. Kroodsma, D. A.; Field, C. B. *Ecol. Appl.* **2006**, *16*, 1975–1985.
12. Hutson, S. S.; Barber, N. L.; Kenny, J. F.; Linsey, K. S.; Lumia, D. S.; Maupin, M. A. Estimated Use of Water in the United States in 2000; USGS Circular 1268, revised 2005.
13. The California Irrigation Management Information System (CIMIS), *CIMIS Equations*; URL http://www.cimis.water.ca.gov/cimis/infoEtoEquation.jsp.
14. Smart, D. R.; Schwass, E.; Morano, L.; Lakso Alan, N. Grapevine root distributions: A comprehensive analysis and a review. In *Soil Environment and Vine Mineral Nutrition*, San Diego, California; Christensen, L. P., Smart, D. R., Roberts, D., Anamosa, P., Eds.; American Society of Enology and Viticulture: San Diego, California, 2005; pp 153−173.
15. Smart, D. R.; Carlisle, E.; Goebel, M.; Alonso Nunez, B. *Plant Cell Environ.* **2005**, *28*, 157–166.
16. Lee, J.; Hopmans, J. W.; van Kessel, C.; King, A. P.; Evatt, K. J.; Louie, D.; D.E., R.; Six, J. *Agric. Ecosyst. Environ.* **2009**, *129*, 378–390.
17. Eissenstat, D. M.; Lakso, A. N.; Neilsen, D.; Smart, D. R.; Bauerle, T. L.; Comas, L. H.; Neilsen, G. H. *Acta Hortic.* **2006**, *721*, 21–26.
18. Schwankl, L.; Hanson, B.; Prichard, T. *Micro-Irrigation of Trees and Vines*; Water Management Handbook Series Division of Agriculture and Natural Resources, publication No. 93-03: Davis, 1996; p 138.
19. Khalil, K.; Mary, B.; Renault, P. *Soil Biol. Biochem.* **2004**, *36*, 687–699.
20. Conrad, R. In *Trace Gas Exchange In Forest Ecosystems*; Gasche, R.; Papen, H.; Rennenberg, H., Ed. Springer: New York, 2002; pp 3−33.
21. Wood, D. W.; Setubal, J. C.; Kaul, R.; Monks, D. E.; Kitajima, J. P.; Okura, V. K.; Zhou, Y.; Chen, L.; Wood, G. E.; Almeida, N. F.; Woo, L.; Chen, Y. C.; Paulsen, I. T.; Eisen, J. A.; Karp, P. D.; Bovee, D.; Chapman, P.; Clendenning, J.; Deatherage, G.; Gillet, W.; Grant, C.; Kutyavin, T.; Levy, R.; Li, M. J.; McClelland, E.; Palmieri, A.; Raymond, C.; Rouse, G.; Saenphimmachak, C.; Wu, Z. N.; Romero, P.; Gordon, D.; Zhang, S. P.; Yoo, H. Y.; Tao, Y. M.; Biddle, P.; Jung, M.; Krespan, W.; Perry, M.; Gordon-Kamm, B.; Liao, L.; Kim, S.; Hendrick, C.; Zhao, Z. Y.; Dolan, M.; Chumley, F.; Tingey, S. V.; Tomb, J. F.; Gordon, M. P.; Olson, M. V.; Nester, E. W. *Science* **2001**, *294*, 2317–2323.
22. Casciotti, K. L.; Sigman, D. M.; Hastings, M. G.; Bohlke, J. K.; Hilkert, A. *Anal. Chem.* **2002**, *74*, 4905–4912.
23. Smith, M. S. *Appl. Environ. Microbiol.* **1983**, *45*, 1545–1547.
24. Burger, M.; Matiasek, M. In *Nitrous Oxide Emissions Research Progress*; Sheldon, A. I., Barnhart, E. P., Eds.; Nova Science Publishers, Inc.: New York, NY, 2009; pp 1−9.
25. Butterbach-Bahl, K.; Kesik, M.; Miehle, P.; Papen, H.; Li, C. *Plant Soil* **2004**, *260*, 311–329.
26. Firestone, M.; Davidson, E. In *Exchange of Trace Gases Between the Terrestial Ecosystem and the Atmosphere*; Andreae, M. O., Shimel, D. S., Eds.; John Wiley & Sons: New York, 1989; pp 7−21.
27. Kesik, M.; Brüggemann, N.; Forkel, R.; Kiese, R.; Knoche, R.; Li, C.; Seufert, G.; Simpson, D.; Butterbach-Bahl, K. *J. Geophys. Res* **2006**, *111*.
28. Burford, J. R.; Bremner, J. M. *Soil Biol. Biochem.* **1975**, *7*, 389–394.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

29. Bowman, R. A.; Focht, D. D. *Soil Biol. Biochem.* **1974**, *6*, 297–301.
30. Bremner, J. M.; Shaw, K. *J. Agric. Sci.* **1958**, 40–52.
31. Duxbury, J. M.; Bouldin, D. R.; Terry, R. E.; Tate, R. L. *Nature* **1982**, *298*, 462–464.
32. Goodroad, L. L.; Keeney, D. R. *J. Environ. Qual.* **1984**, *13*, 448–452.
33. Stanford, G.; Vanderpol, R. A.; Dzienia, S. *Soil Sci. Soc. Am. J.* **1975**, *39*, 284–289.
34. Robertson, G. P.; Tiedje, J. M. *Soil Biol. Biochem.* **1987**, *19*, 187–193.
35. Pluth, D. J.; Nommik, H. *Acta Agric. Scand., Sect. B* **1981**, *31*, 235–241.
36. Pang, P. C. K.; Cho, C. M. *Soil Sci. Soc. Am. J.* **1984**, *48*, 393–399.
37. Davidson, E. A.; Keller, M.; Erickson, H. E.; Verchot, L. V.; Veldkamp, E. *Bioscience* **2000**, *50*, 667–680.
38. Davidson, E. A. In *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides and Halomethanes*; Rogers, J. E., Whitman, W. B., Eds.; Am. Soc. for Microbiol: Washington, D. C., 1991; pp 219−235.
39. Højberg, O.; Revsbech, N. P.; Tiedje, J. M. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1691–1698.
40. Smart, D. R.; Penuelas, J. *Appl. Soil Ecol.* **2005**, *28*, 247–257.
41. Steenwerth, K. L.; Pierce, D. L.; Carlisle, E. C.; Spencer, R. B.; Smart, D. R. *Soil Sci. Soc. Am. J.* **2010**, *74*, 231–239.
42. Smart, D. R.; Ritchie, K.; Stark, J. M.; Bugbee, B. *Appl. Environ. Microb.* **1997**, *63*, 4621–4624.
43. Hart, S. C.; Stark, J. M.; Davidson, E. A.; Firestone, M. K. *Nitrogen mineralization, immobilization and nitrification*, Methods of soil analysis. Part 2; SSSA: Madison, WI, 1994; Vol. 269−290.
44. Hao, X.; Chang, C.; Carefoot, J. M.; Janzen, H. H.; Ellert, B. H. *Nutr. Cycling Agroecosyst.* **2001**, *60*, 1–8.
45. Velthof, G. L.; Oenema, O. *Eur. J. Soil Sci.* **1995**, *46*, 541–549.
46. Christensen, S. *Soil Biol. Biochem.* **1983**, *15*, 531–536.
47. Flessa, H.; Dorsch, P.; Beese, F. *J. Geophys. Res.* **1995**, *100*, 23115–23124.
48. Clayton, H.; McTaggart, I. P.; Parker, J.; Swan, L.; Smith, K. A. *Biol. Fertil. Soils* **1997**, *25*, 252–260.
49. Thomson, P. E.; Parker, J. P.; Arah, J. R. M.; Clayton, H.; Smith, K. A. *Soil Sci. Soc. Am. J.* **1997**, *61*, 1323–1330.
50. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. *Global Biogeochem. Cycles* **2002**, *16*.
51. Dong, Y. S.; Scharffe, D.; Domroes, M.; Qi, Y. C.; Zhang, S. *J. Environ. Sci.* **2000**, *12*, 463–468.
52. Paul, E. A.; Clark, F. E. *Soil Microbiology and Biochemistry*; Academic Press: San Diego, CA, 1996; p 340.
53. Federer, C. A.; Klemedtsson, L. Some factors limiting denitrification in slurries of acid forest soils. *Scand. J. For. Res.* **1988**, *3*, 425–435.
54. Ambus, P.; Christensen, S. *J. Geophys. Res.* **1994**, *99*, 16549–16555.
55. Christensen, S.; Simkins, S.; Tiedje, J. M. *Soil Sci. Soc. Am. J.* **1990**, *54*, 1608–1613.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

56. Drury, C. F.; McKenney, D. J.; Findlay, W. I. *Soil Sci. Soc. Am. J.* **1992**, *56*, 776–770.
57. Robertson, K. *J. Environ. Qual.* **1994**, *23*, 805–809.
58. Groffman, P. M.; Tiedje, J. M. *Soil Biol. Biochem.* **1991**, *23*, 299–302.
59. Weier, K. L.; Doran, J. W.; Power, J. F.; Walters, D. T. *Soil Sci. Soc. Am. J.* **1993**, *57*, 66–72.
60. Myrold, D. D.; Tiedje, J. M. *Soil Biol. Biochem.* **1985**, *17*, 819–822.
61. Kaiser, E. A.; Kohrs, K.; Kucke, M.; Schnug, E.; Heinemeyer, O.; Munch, J. C. *Soil Biol. Biochem.* **1998**, *30*, 1553–1563.
62. Kammann, C.; Grunhage, L.; Muller, C.; Jacobi, S.; Jager, H. J. *Environ. Pollut.* **1998**, *102*, 179–186.
63. Dobbie, K. E.; McTaggart, I. P.; Smith, K. A. *J. Geophys. Res.* **1999**, *104*, 26891–26899.
64. Ruser, R.; Flessa, H.; Schilling, R.; Beese, F.; Munch, J. C. *Nutr. Cycling Agroecosyst.* **2001**, *59*, 177–191.
65. Smith, K. A.; Thomson, P. E.; Clayton, H. *Atmos. Environ.* **1998**, *32*, 3301–3309.
66. WagnerRiddle, C.; Thurtell, G. W.; Kidd, G. K.; Beauchamp, E. G.; Sweetman, R. *Can. J. Soil Sci.* **1997**, *77*, 135–144.
67. Dobbie, K. E.; Smith, K. A. *Global Change Biol.* **2003**, *9*, 204–218.
68. Denmead, O. T.; Freney, J. R.; Simpson, J. R. *Soil Sci. Soc. Am. J.* **1979**, *43*, 726–728.
69. Bremner, J. M.; Robbins, S. G.; Blackmer, A. M. *Geophys. Res. Lett.* **1980**, *7*, 641–644.
70. Conrad, R.; Seiler, W.; Bunse, G. *J. Geophys. Res.* **1983**, *88*, 6709–6718.
71. Mosier, A. R.; Parton, W. J.; Hutchinson, G. L. *Modelling nitrous oxide evolution from cropped and native soils*, Ecological Bulletins Oikos Editorial Office: Stockholm, 1983; Vol. 35.
72. Shepherd, M. F.; Barzetti, S.; Hastie, D. R. *Atmos. Environ.* **1991**, *25A*, 1961–1969.
73. Velthof, G. L.; Jarvis, S. C.; Stein, A.; Allen, A. G.; Oenema, O. *Soil Biol. Biochem.* **1996**, *28*, 1215–1225.
74. Yamulki, S.; Goulding, K. W. T.; Webster, E. A.; Harrison, R. M. *Atmos. Environ.* **1995**, *29*, 1627–1635.
75. Arah, J. R. M.; Smith, K. A.; Crichton, I. J.; Li, H. S. *J. Soil Sci.* **1991**, *42*, 351–367.
76. Wall, L. G.; Tank, J. L.; Royer, T. V.; Bernot, M. J. *Biogeochemistry* **2005**, *76*, 85–111.
77. Skiba, U.; McTaggart, I. P.; Smith, K. A.; Hargreaves, K. J.; Fowler, D. *Energy Convers. Manage.* **1996**, *37*, 1303–1308.
78. Henault, C.; Devis, X.; Page, S.; Justes, E.; Reau, R.; Germon, J. C. *Biol. Fert. Soils* **1998**, *26*, 199–207.
79. Davidson, E.; Verchot, L. V. *Global Biochem. Cycles* **2000**, *14*, 1035–1043.
80. Matson, P. A.; Vitousek, P. M.; Schimel, D. *Regional extrapolation of trace gas flux based on soils and ecosystems*, Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere; John Wiley & Sons: New York, NY, 1989.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

81. Robertson, G. P. In *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*; Rolston, D. E., Ed. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America.: 1993; Vol. Special Publication No, 55, pp 95−108.
82. Konda, R.; Ohta, S.; Ishizuka, S.; Arai, S.; Ansori, S.; Tanaka, N.; Hradjono, A. *Soil Biol. Biochem.* **2008**, *40*, 3021–3030.
83. Turner, D. A.; Chen, D.; Galbally, I. E.; Leuning, R.; Edis, R. B.; Li, Y.; Kelly, K.; Phillips, S. *Plant Soil* **2008**, *309*, 77–88.
84. Folorunso, O. A.; Rolston, D. E. *Soil Sci. Soc. Am. J.* **1984**, *48*, 1214–1219.
85. Pennock, D. J.; van Kessel, C.; Farrell, R. E.; Sutherland, R. A. *Soil Sci. Soc. Am. J.* **1992**, *56*, 770–776.
86. Li, C.; Aber, J. D.; Stange, F.; Butterbach-Bahl, K.; Papen, H. *J. Geophys. Res.* **2000**, *105*, 4369–4384.
87. Christensen, S. *Soil Sci. Soc. Am. J.* **1985**, *54*, 1608–1613.
88. Ball, B. C.; Horgan, G. W.; Parker, J. P. *Eur. J. Soil Sci.* **2000**, *51*, 607–616.
89. Schwankl, L. J.; Edstrom, J. P.; Hopmans, J. W.; Andreu, L.; Koumanov, K. S. *Calif. Agric.* **1999**, 39–43.
90. Prichard, T. L. *A volume balance approach to quality wine grape irrigation*; Viticultural Practices University of California Cooperative Extension: Davis, California USA, 1992.
91. Andreu, L.; Hopmans, J. W.; Schwankl, L. *Agric. Water Manage.* **1997**, *35*, 123–146.
92. Wilhelm, E.; Battino, R.; Wilcock, R. J. *Chem. Rev.* **1977**, *77*, 219–260.
93. Steenwerth, K. L.; Belina, K. M. *Appl. Soil Ecol.* **2008**, *40*, 370–380.
94. Steenwerth, K. L.; Belina, K. M. *Agric. Ecosyst. Environ.* **2010**, *138*, 127–131.
95. Suddick, E. M.; Scow, K. M.; Horwath, W. R.; Jackson, L. E.; Smart, D. R.; Mitchell, J.; Six, J. *Adv. Agron.* **2010**, *107*, 123–167.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch013

Chapter 14

Global Nitrous Oxide Emissions: Sources and Opportunities for Mitigation

R. M. Rees[*]

Scottish Agricultural College Edinburgh, EH9 3JG, U.K.
[*]E-mail: Bob.rees@sac.ac.uk

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

Global emissions of nitrous oxide (N_2O) have risen steadily in recent years as a result of human activity. During the 1990s, total emissions were estimated to be 28 Tg N_2O annually. Nitrous oxide is a powerful greenhouse gas and in addition is involved in the destruction of stratospheric ozone. Emissions are spatially uneven and are strongly dominated by sources from fertilised agricultural soils, both in the form of direct and indirect emissions. Soil conditions, particularly at the time of fertiliser application, are important in determining the magnitude and timing of emissions. The type of land use is also important, with a strong correlation between livestock farming and national emissions. Opportunities exist to reduce emissions of N_2O by improving the efficiency of nitrogen (N) use in farming systems and the application of new management technologies. Such approaches are often popular with farmers given that they contribute to environmental and economic benefits. However, to achieve large emission reductions it is necessary to alter the nature of production systems, with particular attention being focussed on livestock production. This paper reviews the global anthropogenic sources of emission of N_2O and considers options for mitigation at a regional scale.

Introduction

Nitrous oxide (N_2O) is a powerful greenhouse gas with a global warming potential of 296 times greater than that of CO_2 (*1*). For this reason it is recognised

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

that efforts to limit the accumulation of greenhouse gases in our atmosphere must include measures that reduce N_2O emissions (*2*). Sources of N_2O are diverse, but the dominant source is of terrestrial origin. Total global emissions during the 1990s were estimated by the IPCC's Fourth Assessment Report to be 27.8 (13.4-43.5) Tg N_2O per year (*3*). This report recognises that there is considerable uncertainty in some emission estimates of N_2O and that less than half of the global N_2O emissions are directly attributable to anthropogenic sources. However, anthropogenic sources have been primarily responsible for the growth in emissions over the past century, and they are most easily reduced through mitigation measures. The remainder of this chapter therefore discusses the nature and potential mitigation of anthropogenic N_2O sources. The largest single anthropogenic source (27% of total global anthropogenic emissions) originates directly from soils mostly following fertiliser nitrogen applications and other land based sources can be linked to the management of nitrogen in agricultural systems (Figure 1). These include manures in pasture based systems (19%), indirect losses (9%), savanna burning 7% and indirect N_2O from non agricultural NOx (6%), with total anthropogenic sources in 2005 contributing to 9.6 Tg N_2O per year (*4*).

Although the source processes that generate N_2O are well understood (*6–9*), it remains difficult to predict emissions in the field given the strong interaction of environmental drivers that change the rates of emissions, often over short timescales and small spatial scales. A meta-analysis of research studies has shown that N_2O emissions vary according to the amount, chemical form and timing of fertiliser nitrogen (N) applications, but soil conditions such as wetness, pH and drainage are also important (*10*).

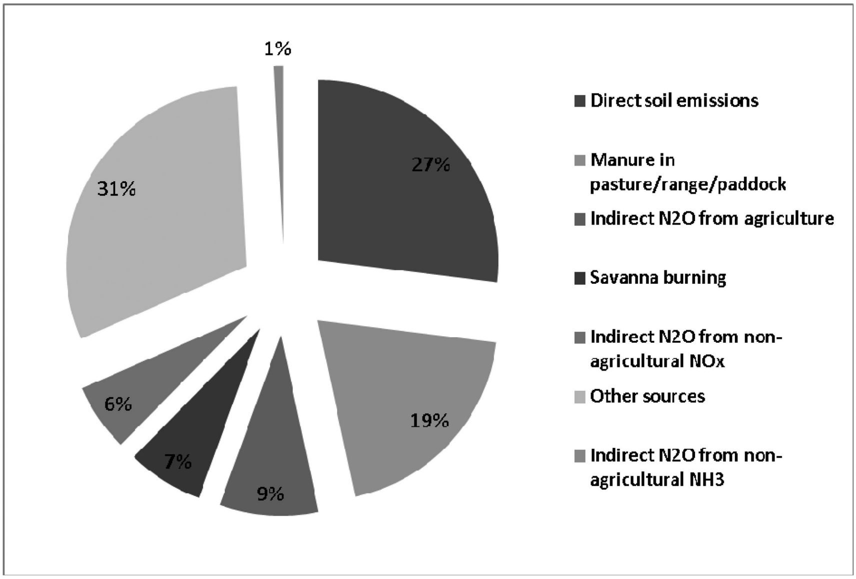


Figure 1. Global anthropogenic sources of N_2O partitioned by source. The other category covers a range of industrial and terrestrial sources including chemical production, transport, energy production and biomass burning (4, 5).

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

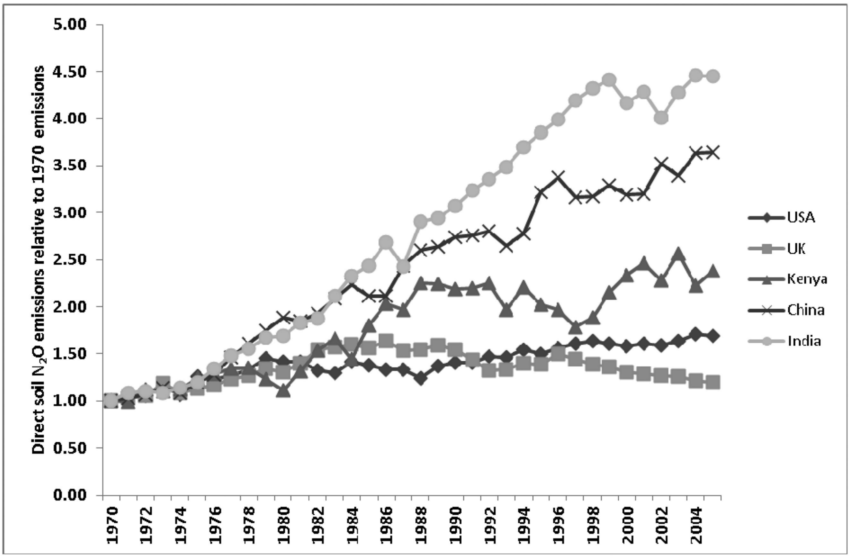


Figure 2. Growth rates in direct soil emissions of N_2O compared against a 1970 baseline from selected countries between 1970-2005. (4, 5)

The variability in emissions associated with environmental conditions and management activity provide considerable scope for mitigation of N_2O emissions. It has been suggested that the application of improved management practices and better fertiliser management could reduce global emissions by 20% (*11*), and provide co-benefits of improved nutrient use efficiency, reduced leaching losses and increased profitability for farming enterprises. However, the realisation of this mitigation potential needs to take account of large regional differences in the sources of emissions and the technological and economic potential of countries to take action.

During the past century, the use of nitrogen fertilisers has increased significantly in order to support growing human populations and their demand for food (*12*, *13*). However, this growth has been very uneven over the past 30 years with high population growth in the developing regions of the world, linked to large increases in fertiliser use and associated N_2O emissions. A comparison of emission inventories from different countries over the period between 1970-2005 illustrates that whilst N_2O emissions in developed countries such as the UK and the US have been relatively stable, in developing regions such as China and India, emissions over the period increased by between three to four times (Figure 2). The growth in fertiliser use and associated N_2O emissions are predicted to continue with continuing regional variability (*14*).

Regional differences in emissions of N_2O from agriculture can be described in terms of the amount per region and also the way in which that amount is partitioned by source. At the global scale, Asia is the dominant source of N_2O contributing to over 45% of anthropogenic emissions (Figure 3). This is greater than the combined emissions of Africa, South and Central America, and Europe and Oceana, reflecting the large human population in this region and their consumption of fertiliser nitrogen to support food production. It should also be noted that there are significant differences in partitioning of sources of N_2O between regions. Thus in Europe, Asia, North America, and Central and South America, direct emissions from soils make up over 50% of total emissions. This reflects the importance of emissions from crop growth in these areas. In Africa and Oceana by contrast emissions from manure and pasture management are dominant.

Both the amount and intensity of fertiliser use also vary significantly by region (Table 1). Highest intensities of N use (between 26-24 kg N/ha) are located in Europe, North America and Asia, however, these values represent average N applications per unit area of agricultural land, and hide significant variability. Much lower rates of fertiliser N are applied to regions of the world that include extensive (often unfertilised) grassland or rangeland landscapes in Africa, Latin America and Oceana. The larger land area and higher fertiliser use in Asia result in the largest regional N_2O emission of 2451 Gg/year (Table 2). But the larger population of Asia contributes to the lowest global emission (623 g N_2O/person/year) when expressed on a per capita basis. This compares with emissions in Latin America and North America of 1521 and 2167 g N_2O/person/year, respectively. The projected population growth to 9 billion by the middle part of the century (UN median projections) can be used to predict N_2O emissions by 2050 assuming a constant per capita emission. The projections would indicate very large increases in emissions in Africa and Asia, but falling emissions across Europe.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

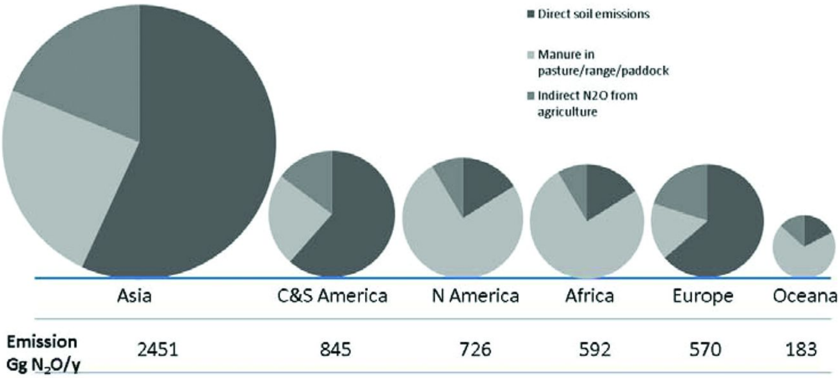


Figure 3. Global N_2O emissions from agriculture divided by continent and partitioned by source. The size of the pies is proportional to the annual emission in 2005 (4, 5).

Table 1. Fertiliser use and land areas in different regions of the world for 2005 (*15*)

Region[1]	*Fertiliser N use (Mt N)*	*Total Area (000 k ha)*	*Agricultural Area (000 k ha)*	*Mean N application to agricultural area kg N/ha*
Africa	3.1	30312	1151	2.7
Asia	55.1	31967	1640	33.6
Europe	13.0	2300	472	27.5
Latin America and Caribbean	5.8	2052	713	8.2
N America	12.8	2002	480	26.6
Oceana	1.3	856	459	2.8

Table 2. Regional anthropogenic N_2O emissions per capita emissions and projected growth rates (*5*, *15*)

	Population	*Current N_2O emission (Gg)*	*Current per capita emission of N_2O (g)*	*Projected population growth 2000-2050*	*Projected N_2O emission 2050 (Gg)*
Africa	921073	592	643	2.44	1444
Asia	3936536	2451	623	1.41	3467
Europe	729421	570	781	0.95	542
Latin America & Caribbean	556512	846	1521	1.40	1184
N America	335175	726	2167	1.41	1022

At the global level, the production of N_2O emissions is closely linked to meat production (Figure 4) and this helps to explain the high per capita emissions on the American continent where meat production is highest. Such observations have been previously reported (*16–18*), but the relationship is important when considering future trends in emissions and potential for mitigation. As illustrated above, emissions of N_2O are already dominated by Asia, where per capita meat consumption is relatively low when compared to that of regions such as Europe and North America. It is widely assumed that as the populations of Asia become more affluent, consumption of meat and dairy products will increase. Such a change would almost inevitably increase N_2O emissions from this region still further.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

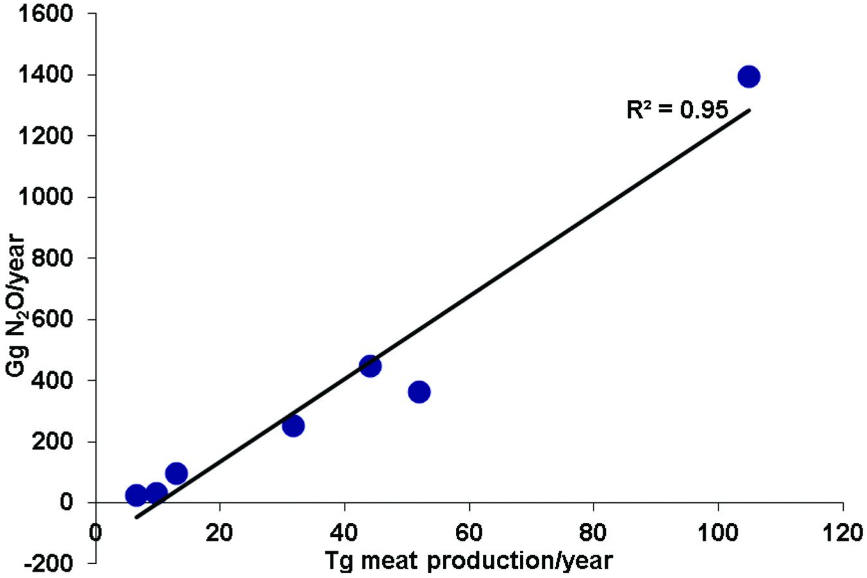


Figure 4. The relationship between direct soil emissions of N_2O and meat production (5, 15).

The accounting system used to assign emissions to individual regions has weaknesses when used to consider mitigation potential on a regional basis. Emissions are assigned to the country in which agricultural products are produced. However, the global trade in agricultural products generates major flows of commodities between regions. For example, livestock feed consumed in North America and Europe is produced in large quantities in South America, with an annual transfer of N in grain of 2.4 Mt (*19*). Despite these inadequacies, the link between N_2O emission and livestock production is well-established, and it is likely that the projected increase in the consumption in Asia is inconsistent with attempts to reduce N_2O emissions in the coming decades.

Mitigation

The opportunities for mitigation of N_2O emissions from agriculture will vary according to region as a consequence of large differences in methods of production within farming systems, and in both technology and resources available for the application of mitigation measures. The potential for mitigation will also vary, being large in circumstances where high levels of fertiliser N are applied to highly organic soils, but much lower when N inputs are low and other soil conditions constrain emissions. A wide range of mitigation measures have been proposed, each associated with varying mitigation potentials (Table 3). It is widely recognised that those options that improve the efficiency of resource use within agriculture are most likely to be adopted as a priority, since they bring the co-benefits of economic gain and wider environmental benefits (*49*). Beyond improvements in efficiency, there are a range of technical and management changes that can be used to reduce N_2O emissions such as the replacement of nitrogen fertilisers by biologically fixed N from legumes within farming systems (*50*, *51*), the use of nitrification inhibitors (*40*), drainage (*52*) and improved soil conditions (*38*, *53*). Such approaches are likely to deliver modest reductions in emissions of between 10-20%. Greater emission reductions are likely to be possible only through more significant land use change, involving a switch to systems with lower inputs of fixed nitrogen and reductions in some areas of livestock production. The benefits of such changes would however vary on a regional basis.

Food Supply

Increases in the global population are driving a rapid increase in demand for food. With the global population predicted to peak at around 9 billion by the middle part of this century, demand is currently rising steeply. At the same time, the increasing affluence of the world's population is resulting in the demand for higher value products associated with higher greenhouse gas emissions (e.g. meat and dairy products). However, agriculture is also facing constraints generated by the limited availability of land, limited resources (such as oil and phosphorus), limited water availability, declining biodiversity and climate change. These factors combined contribute to what has been described as "the perfect storm" for agriculture (*54*). One of the key messages from this analysis is that future methods of food production need to rely on more sustainable approaches to the management of resources, and in particular, there is a need to produce food with significantly lower greenhouse gas emissions. It has been argued that one approach to this problem would be to develop the concept of sustainable intensification (*54*). This would be achieved by dramatic increases in the efficiency with which resources in agriculture are used enabling production to be maintained or increased whilst resource inputs decline. In theory there is plenty of scope for improvement. It has been found that only 14% of the N fixed by the Harber-Bosch process is consumed by humans with a vegetarian diet. This falls to 4% for a carnivorous diet (*12*).

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

Costs

The costs of different mitigation options vary significantly. This variability is associated both with the magnitude of intervention involved, and the location in which it takes place. Thus alteration in the timing of fertiliser nitrogen applications or improved adherence to fertiliser recommendations may involve little or no cost to a farmer and could even contribute to improvements in productivity. Such measures are always likely to be the easiest to introduce and contribute quickly to reductions in greenhouse gas emissions. More significant savings in emissions may require interventions involving a greater change in methods of production, or greater cost. For example improved drainage has been shown in many circumstances to reduce N_2O emissions following addition of fertiliser nitrogen. However, such activities can be highly expensive and are often justified only where increases in crop yield can be demonstrated. The relationship between the cost of a mitigation measure and greenhouse gas savings, can be represented by preparing a marginal abatement cost curve. Recent work in the UK has shown that a large amount of greenhouse gas mitigation can be achieved by applying measures that deliver both financial savings and reductions in greenhouse gas emissions; so called win-win measures (*49*). The analysis takes into account both the cost of the measure and the costs of impacts associated with it (e.g., changes in the value of agricultural products). This work implies that improvements in efficiency can make an important contribution to reducing greenhouse gas emissions from the agricultural sector. The approach is also valuable in identifying a logical order in which mitigation activities should be implemented. However, it can be difficult to assess the importance of individual mitigation measures on greenhouse gas balances, particularly at larger regional scales. It is also difficult to determine how individual measures will interact when used in combination (*55*). It could be envisaged that a farm enterprise aiming to reduce its greenhouse gas emissions would implement several measures simultaneously. However, once each measure has been introduced the potential to mitigation by the introduction of further measures becomes less, and the potential costs increase. A further difficulty relates to spatial heterogeneity. At a national scale, if a government wishes to reduce emissions of greenhouse gases, it may be more appropriate to target emission hotspots rather than attempt to introduce blanket measures that could involve significant cost and yet relatively low mitigation. However, within hotspots, more significant intervention could achieve a high level of mitigation and remain cost-effective at the national scale.

There is also likely to be variation in the costs of measures in different regions. Thus where labour costs are low, such as in many developing countries, activities involving additional labour (cultivation or increasing numbers of fertiliser applications) may result in higher greenhouse gas savings per unit cost than elsewhere.

Table 3. The range of potential N_2O mitigation achieved by the use of different measures

Category	*Measure*	*Mitigation potential (% reduction in business as usual)*	*Reference*
Agronomy	Crop mixtures and intercrops	0-20	(*20*)
	More efficient crop varieties	0-20	(*21*)
	Improved management of crop residues	10-30	(*22–25*)

Continued on next page.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

Table 3. (Continued). The range of potential N_2O mitigation achieved by the use of different measures

Category	*Measure*	*Mitigation potential (% reduction in business as usual)*	*Reference*
	Use of legumes to provide N input	20-40	(*26*)
	Improved irrigation scheduling	0-20	(*27*, *28*)
Soil Management	Minimum tillage	-20-+10	(*29–32*)
	Improved drainage	0-20	(*33–35*)
	pH management	0-20	(*36*)
	Improved soil structural conditions	0-20	(*37*, *38*)
Fertiliser Management	Use of urea in place of ammonium nitrate	0-10	(*39*)
	Nitrification inhibitors	20-80	(*40–42*)
	Reduced fertiliser application	10-80	(*43*, *44*)
	Improved timing	0-10	(*43*, *45*)
	Precision application of fertilisers	10-20	(*11*)
	Improved management of manures and composts	10-20	(*46*)
Land use change	Grassland to cropland	10-40	(*47*)
	Grassland to agro-forestry	20-40	(*48*)
	Cropland to agro-forestry	20-40	(*48*)

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

Regional Potential for Mitigation

Europe

Both total (570 Gg/year) and per capita (781g/person/year) emissions of N_2O in Europe are not high by global standards. However, fertiliser nitrogen application rates in Europe are relatively high when compared with global averages. Agricultural systems are generally dependent upon high levels of technical support and sophisticated advisory and development systems. Over the past decade, rates of fertiliser nitrogen application have declined in response to high fertiliser costs, environmental regulation and attempts to reduce greenhouse gas emissions, but reducing emissions of N_2O remains a high priority for many European countries. A recent analysis of the greenhouse gas balance in Europe identified N_2O as being of particular importance (*2*). Emissions of N_2O and CH_4 from land based sources in Europe effectively cancels out the carbon sequestration capacity of forests and grasslands maintaining a near neutral greenhouse gas balance. However, future intensification in the region could easily lead to the continent becoming a net source as a result of non-CO_2 greenhouse gas emissions (*2*). Nitrogen use in Europe is also influenced by European agricultural support policies. Over the past decade the nitrates directive has encouraged more efficient use and lower levels of nitrogen application to farmland in order to reduce nitrate leaching within catchments. The high levels of nitrogen use, and sophisticated support mechanisms provide the opportunity for further reductions in N_2O emissions through a range of measures. In the first instance increasing efficiency is likely to provide an opportunity for reductions in N_2O emissions, leading to 20 to 40% reduction in some circumstances (*55*). Larger emission reductions are likely to be possible through land use change. However, Europe also has the opportunity for technical intervention within agricultural systems that are not possible elsewhere due to the high levels of technical capability. Thus the use of nitrification inhibitors, precision farming, and the development of new crop varieties can contribute to significant further reductions in emissions although often that higher cost.

Asia

Asia dominates emissions of N_2O at the global level, however, per capita emissions are the lowest in any region (623 g/person/year). Asia currently emits 2451 Gg N_2O/year or 46 % of the global anthropogenic total, and so is hugely important in determining the magnitude of global emissions. In 2005 Asia used 55 Mt N which was equivalent to 60% of the global total. The observation that the proportion of global N_2O emissions is so much lower that the proportion of fertiliser use could be seen as an indicator of efficiency, and is explained by the lower consumption of meat based food products in this region. Emissions in India and China are rising rapidly in response to fertiliser applications to support increasing food production. Emissions are largely associated with direct losses from soils, indicating the importance of losses from fertiliser nitrogen application to crops. A recent modelling exercise explored the distribution of N_2O emissions in China, and found a highly variable distribution, which was explained

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

by the density of cropping and fertiliser use (*56*). A regional modelling study indicated that China's grasslands also make an important contribution of around 77 Gg N_2O/year to national emissions (*57*). The larger fertiliser applications and warmer summers in central and south eastern China were associated with highest emissions, and this is an area in which mitigation measures would be most effective. Indian N_2O emissions also show a wide variability, and were similarly related to the distribution of N inputs (*58*).

Investment in agricultural support systems in these regions is relatively low, providing significant opportunities for increased fertiliser use efficiency based upon improved advice and consultancy (*59*). This would include recommendations that enable crop demand for nitrogen to be more accurately matched to fertiliser supply. Extension services could also provide recommendations on improved agronomy and soil science.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

Africa

Africa has relatively low emissions of N_2O (592 Gg in 2005) and low per capita emissions (643g/person/year). There is a scarcity of data describing emissions in response to agricultural management across the continent (*60*), however, they are low when compared to those in other regions. This could be because of high levels of infertility within soils, low rainfall across large regions of the continent, and low fertiliser application rates. Studies in Zimbabwe have reported relatively low emissions of 3.4 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$ from croplands, but observed much higher emissions (30.5 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$) from cleared woodlands (*61*). Reviews of other studies have also indicated that low emissions are widespread across the African continent (*62*). Extension services in this region are relatively poor, providing an opportunity for investment targeted at increasing efficiency of fertiliser use. Chronic malnutrition and hunger across the region also place urgent demands upon extension services to increase agricultural productivity in order to achieve higher levels of food production across the continent. There is an urgent need to address these problems through integrated nutrient management which includes developing an appropriate balance of organic and inorganic nutrient inputs that avoid the long term depletion of the soil nutrient capital (*63*, *64*).

North America

Emissions of N_2O from North America were 726 Gg N_2O/year which translates into per capita emission of 2167 g N_2O/year, the equivalent of 646 kg CO_2/year. The land area in North America and the area under cultivation is large, but fertiliser application rates per unit area are lower than those in other developed regions such as Europe. Like Europe, North America has a well-developed extension service, and the high-tech agricultural industry. This provides opportunities for reducing N_2O emission through increasing fertiliser use efficiency such as improving timing and rates of fertiliser applications, improving soil conditions, and agronomy (*65*). The application of high-tech solutions to fertiliser management such as the use of precision farming and nitrification inhibitors also provide important opportunities in North America for reducing emissions. High levels of meat production and consumption contribute significantly to emissions in North America, and therefore significant emission reductions could be achieved by lowering levels of meat production across the continent.

Snyder *et al.* (*65*) identified four areas that would assist in the minimisation of greenhouse gas emissions from US agriculture. These were general adherence to best agronomic practice, maintenance of application equipment, efficient crop management and system planning, and the use of urease and nitrification inhibitors. In a review of greenhouse gas mitigation practices (*66*) highlighted the importance of pollution swapping as a consequence of some measures. Thus for example reduced tillage and the incorporation of manures and slurry centre soils can contribute to increased carbon storage; however, this is often outweighed by increase in N_2O emissions.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

South and Central America

Emissions of N_2O in this region were 846 Gg/year, with per capita emissions of 1521 g N_2O/year. These relatively large emissions reflect the importance of livestock production in the extensive rangeland ecosystems located across South America. No-till farming systems are thought to reduce net greenhouse gas emissions through increasing C sequestration, and are widely adopted in the South American pampas. However, a review of experiments has shown that increased N_2O emissions resulting from no till offset the benefits of C sequestration (*67*). It is anticipated that population growth and the associated demand for food will lead to rapid growth in N_2O emissions in the continent of South America (*68*).

Land use change has historically been an important driver of greenhouse gas emissions on the South American continent, particularly in areas such as Brazil, where widespread deforestation has taken place in order to accommodate large areas of grain production. More recently sugarcane has replaced other crops in Brazil as being the most important in terms of area and income, reflecting the growing importance of bio-ethanol production as an output from agricultural systems. An understanding of the greenhouse gas emissions associated with biofuel production has become particularly important since it determines the extent to which such products can offset greenhouse gas emissions by fossil fuels. Thus the production of crops, such as sugarcane, grain crops, and oilseeds, is associated with greenhouse gas emissions mainly in the form of N_2O emissions. When these emissions exceed those who would be associated with the combustion of an equivalent amount of fossil fuel, it is argued that such production has a negative environmental impact. Research has shown that production of biofuels in warmer tropical countries such as Brazil is associated with relatively high levels of efficiency, allowing them to contribute to a reduction in net greenhouse gas emissions (*69*).

Oceana

Land area and agricultural production in Oceana are dominated by Australia and New Zealand, with a total N_2O production of 183 Gg/year (the lowest in any region). It should be noted that this region also includes the Pacific islands of Melanesia and Polynesia and is therefore climatically highly diverse with large areas of desert and agricultural land with low productive potential. Parts of New Zealand and Australia include some areas of highly productive intensively managed agricultural land. Nitrous oxide emissions within the region therefore highly variable, and are often influenced strongly by cycles of wetting and drying in the more arid regions of Australia. Some recent studies have indicated that N_2O emissions in these drier areas may be overestimated by the IPCC default emission factors (*70*). New Zealand's agricultural economy is dominated by pasture based on livestock production. This combined with the fact that New Zealand has relatively scarce heavy industry has led to the agricultural sector being the main source of greenhouse gas emissions. New Zealand has therefore placed a high priority on the development of mitigation strategies that can be used to reduce greenhouse gas emissions for the agricultural sector. Recent studies have shown that N_2O emissions can be produced from grazed grasslands by between 50 and 70% by use of nitrification inhibitors (*40*, *71*, *72*). These reductions in N_2O emission were also associated with a reduction in other losses of nitrogen and increasing nitrogen use efficiency. This makes products such as nitrification inhibitors more attractive commercially particularly given the increasing cost of nitrogen fertilisers.

Conclusions

The global growth in N_2O emissions has been driven by an increase in the demand for agricultural produce and of meat and dairy products. There are many options available to producers that can reduce emissions on a unit area and unit product basis. In many circumstances, significant reductions in emissions can be achieved by increasing the efficiency of farming systems. Options include improvements in the timing and amounts of N fertilisers applied, careful management of soil conditions and the use of appropriate crops and crop rotations that match the prevailing environmental conditions. In some developed countries, this may involve reducing N inputs to agricultural systems by improving N fertiliser efficiency, but in some developing countries, increasing the amounts of N fertiliser may deliver lower emissions on a unit product basis.

Minor changes to the management of agricultural systems as described above could be expected to deliver moderate reductions in N_2O emissions, and would be linked to co-benefits in terms of improved economic performance and other environmental benefits. However, larger emission reductions would be likely to require more significant change in land use and production systems. In particular a switch away from the largely meat based diets that are prevalent in North America and Europe would result in significant additional savings. It is interesting to note that such demand led changes would not always be reflected in the national greenhouse gas budgets of countries where those changes occurred,

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

given that international trade results in widespread distortions of the link between greenhouse gas emissions and consumption of agricultural produce. However, as global societies seek ways of reducing greenhouse gas emissions, changes in the efficiency and nature of food production systems around the globe are likely to become hard to resist.

Acknowledgments

Financial support for this work was provided by the Scottish Government.

References

1. Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M; Averyt, K. B.; Tignor, M.; Miller, H. L. *IPCC: Climate Change 2007: The Physical Science Basis*, Report of the Intergovernmental Panel on Climate Change (IPCC); Cambridge University Press: Cambridge, 2007.
2. Schulze, E. D.; Luyssaert, S.; Ciais, P.; Freibauer, A.; Janssens, E. A. *Nat. Geosci.* **2009**, *2*, 842–850.
3. Denman, K. L.; Brasseur, G.; Chidthaisong, A.; Ciais, P.; Cox, P. M.; Dickinson, R. E.; Hauglustaine, D.; Heinze, C.; Holland, E.; Jacob, D.; Lohmann, U.; Ramachandran, S.; da Silva Dias, P. L.; Wofsy, S. C.; Zhang, X. Couplings Between Changes in the Climate System and Biogeochemistry. In *Climate Change 2007: The Physical Science Basis*; Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K. B.; Tignor, M.; Miller, H. L., Eds.; ; Cambridge University Press: Cambridge, U.K., 2007.
4. European Commission, Joint Research Centre (JRC)/Netherlands Environmental Assessment Agency (PBL), 2010.
5. Emission Database for Global Atmospheric Research (EDGAR), Version 4.1. URL http://edgar.jrc.ec.europe.eu.
6. Wrage, N.; Velthof, G. L.; van Beusichem, M. L.; Oenema, O. *Soil Biol. Biochem.* **2001**, *33*, 1723–1732.
7. Mosier, A. R. *Plant Soil* **2001**, *228*, 17–27.
8. Bateman, E. J.; Baggs, E. M. *Biol. Fertil. Soils* **2005**, *41*, 379–388.
9. Skiba, U.; Drewer, J.; Tang, Y. S.; van Dijk, N.; Helfter, C.; Nemitz, E.; Famulari, D.; Cape, J. N.; Jones, S. K.; Twigg, M.; Pihlatie, M.; Vesala, T.; Larsen, K. S.; Carter, M. S.; Ambus, P.; Ibrom, A.; Beier, C.; Hensen, A.; Frumau, A.; Erisman, J. W.; Brggemann, N.; Gasche, R.; Butterbach-Bahl, K.; Neftel, A.; Spirig, C.; Horvath, L.; Freibauer, A.; Cellier, P.; Laville, P.; Loubet, B.; Magliulo, E.; Bertolini, T.; Seufert, G.; Andersson, M.; Manca, G.; Laurila, T.; Aurela, M.; Lohila, A.; Zechmeister-Boltenstern, S.; Kitzler, B.; Schaufler, G.; Siemens, J.; Kindler, R.; Flechard, C.; Sutton, M. A. *Agric., Ecosyst. Environ.* **2009**, *133*, 139–149.
10. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. *Global Biogeochem. Cycles* **2002**, *16*, 1058–1070.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

11. Mosier, A. R.; Duxbury, J. M.; Freney, J. R.; Heinemeyer, O.; Minami, K. *Clim. Change* **1998**, *40*, 7–38.
12. Galloway, J. N.; Cowling, E. B. Reactive nitrogen and the world: 200 years of change. *Ambio* **2002**, *31*, 64–71.
13. Erisman, J. W.; Sutton, M.; Galloway, J. N.; Klimont, Z.; Winiwarter, W. *Nat. Geosci.* **2008**, *1*, 636–639.
14. Tilman, D.; Fargione, J.; Wolff, B.; D'Antonio, C.; Dobson, A.; Howarth, R.; Schindler, D.; Schlesinger, W. H.; Simberloff, D.; Swackhamer, D. *Science* **2001**, *292*, 281–284.
15. Food and Agriculture Organization of the United Nations (FAO). FAOSTAT. URL: http://faostat.fao.org/
16. Steinfeld, H.; Gerber, P.; Wassenaar, T.; Castel, V.; Rosales, M.; de Haan, C. *Livestock's Long Shadow; Environmental Issues and Options*; Rome, Food and Agriculture Organization of the United Nations (FAO), 2006.
17. Galloway, J. N.; Burke , M.; Bradford, G. E.; Naylor, R.; Falcon, W.; Chapagain, A. K.; Gaskell, J. C.; McCullough, E.; Mooney, H. A.; Oleson, K. L. L.; Steinfeld, H.; Wassenaar, T.; Smil, V. *Ambio* **2007**, *36*, 622–629.
18. Garnett, T. *Environ. Sci. Policy* **2009**, *12*, 491–503.
19. Galloway, J. N.; Townsend, A. R.; Erisman, J. W.; Bekunda, M.; Cai, Z. C.; Freney, J. R.; Martinelli, L. A.; Seitzinger, S. P.; Sutton, M. A. *Science* **2008**, *320*, 889–892.
20. Pappa, V. A.; Rees, R. M.; Walker, R. L.; Baddeley, J. A.; Watson, C. A. Effects of intercrops in a three year low input rotation. *Climate, Water and Soil: Science, Policy and Practice*; Crichton, K., Audsley, R., Eds.; SAC/SEPA: Edinburgh, 2010; pp 153−159.
21. Cassman, K. G.; Dobermann, A .; Walters, D. T. *Ambio* **2002**, *31*, 132–140.
22. Aulakh, M. S.; Khera, T. S.; Doran, J. W.; Bronson, K. F. *Biol. Fertil. Soils* **2001**, *34*, 375–389.
23. Promsakha, S.; Sakonnakhon, N.; Toomsan, B.; Cadisch, G.; Baggs, E. M.; Vityakon, P.; Limpinuntana, V.; Jogloy, S.; Patanothai, A. *Plant Soil* **2005**, *272*, 183–199.
24. Baggs, E. M.; Chebii, J; Ndufa, J. K. *Soil Tillage Res.* **2006**, *90*, 69–76.
25. Ciarlo, E. A.; Llorente, M. M.; Conti, M. E.; Giardina, E. B. *Commun. Soil Sci. Plant Anal.* **2009**, *40*, 2756–2772.
26. Soussana, J. F.; Allard, V.; Ambus, P.; Berbigier, P.; Campbell, C.; Cellier, P.; Ceschia, E. *Sources and sinks of greenhouse gases from European grasslands and mitigation options*; XX International Garssland Congress: Dublin, Ireland, 2005; p 564.
27. Vallejo, A.; Diez, J. A.; Lopez-Valdivia, L. M.; Cartagena, M. C.; Tarquis, A.; Hernaiz, P. *Biol. Fertil. Soils* **2004**, *40*, 93–100.
28. Sanchez-Martin, L.; Meijide, A.; Garcia-Torres, L.; Vallejo, A. *Agric., Ecosyst. Environ.* **2010**, *137*, 99–107.
29. Skiba, U.; van Dijk, S.; Ball, B. C. *Soil Use Manage.* **2002**, *18*, 340–345.
30. Elder, J. W.; Lal, R. Tillage effects on gaseous emissions from an intensively farmed organic soil in North Central Ohio. *Soil Tillage Res.* **2008**, *98*, 45–55.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

31. Halvorson, A. D.; Del Grosso, S. J.; Reule, C. A. *J. Environ. Qual.* **2008**, *37*, 1337–1344.
32. Rochette, P. *Soil Tillage Res.* **2008**, *101*, 97–100.
33. Rees, R. M.; Wuta, M.; Furley, P. A.; Li, C. S. *J. Biogeogr.* **2006**, *33*, 424–437.
34. Dobbie, K. E.; Smith, K. A. *Soil Use Manage.* **2006**, *22*, 22–28.
35. Goldberg, S. D.; Knorr, K. H.; Blodau, C.; Lischeid, G.; Gebauer, G. *Global Change Biol.* **2010**, *16*, 220–233.
36. Mosier, A. R.; Delgado, J. A.; Keller, M. Methane and nitrous oxide fluxes in an acid Oxisol in western Puerto Rico: Effects of tillage, liming and fertilization. *Soil Biol. Biochem.* **1998**, *30*, 2087–2098.
37. Smith, K. A.; McTaggart, I. P.; Tsuruta, H. *Soil Use Manage.* **1997**, *13*, 296–304.
38. Ball, B. C.; Scott, A.; Parker, J. P. *Soil Tillage Res.* **1999**, *53*, 29–39.
39. Venterea, R. T.; Dolan, M. S.; Ochsner, T. E. *Soil Sci. Soc. Am. J.* **2010**, *74*, 407–418.
40. Di, H. J.; Cameron, K. C.; Sherlock, R. R. *Soil Use Manage.* **2007**, *23*, 1–9.
41. Fangueiro, D.; Fernandes, A.; Coutinho, J.; Moreira, N.; Trindade, H. *Commun. Soil Sci. Plant Anal.* **2009**, *40*, 3387–3398.
42. Bhatia, A.; Sasmal, S.; Jain, N.; Pathak, H.; Kumar, R.; Singh, A. *Agric., Ecosyst. Environ.* **2010**, *136*, 247–253.
43. Ma, B. L.; Wu, T. Y.; Tremblay, N.; Deen, W.; Morrison, M. J.; Mclaughlin, N. B.; Gregorich, E. G.; Stewart, G. *Global Change Biol.* **2010**, *16*, 156–170.
44. Hoben, J. P.; Gehl, R. J.; Millar, N.; Grace, P. R.; Robertson, G. P. *Global Change Biol.* **2011**, *17*, 1140–1152.
45. Velthof, G. L.; Hoving, I. E.; Dolfing, J.; Smit, A.; Kuikman, P. J.; Oenema, O. *Nutr. Cycling Agroecosyst.* **2010**, *86*, 401–412.
46. Jones, S. K.; Rees, R. M.; Skiba, U. M.; Ball, B. C. *Agric., Ecosyst. Environ.* **2007**, *121*, 74–83.
47. Choudrie, S. L.; Jackson, J.; Watterson, J. D.; Murrells, T.; Passant, N.; Thomson, A.; Cardenas, L. M.; Leech, A.; Mobbs, D. C.; Thistlewaite, G. *UK Greenhouse Gas Inventory, 1990 to 2006*; Annual Report for submission under the Framework Convention on Climate Change. DEFRA. United Nations Framework Convention on Climate Change, 2008.
48. Smith, P.; Goulding, K. W. T.; Smith, K. A.; Powlson, D. S.; Smith, J. U.; Falloon, P.; Coleman, K. *Soil Use Manage.* **2000**, *16*, 251–259.
49. Moran, D.; MacLeod, M.; Wall, E.; Eory, V.; McVittie, A.; Barnes, A.; Rees, R.; Topp, C. F. E.; Moxey, A. *J. Agric. Econ.* **2010**, doi: 10.1111/j.1477-9552.2010.00268.x
50. Rochette, P.; Janzen, H. *Nutr. Cycling Agroecosyst.* **2005**, *73*, 171–179.
51. Drinkwater, L. E.; Wagoner, P.; Sarrantonio, M. Legume-based cropping systems have reduced carbon and nitrogen losses. *Nature* **1998**, *396*, 262–265.
52. Dobbie, K. E.; Smith, K. A. *Global Change Biol.* **2003**, *9*, 204–218.
53. Skiba, U. M.; van Dijk, S.; Ball, B. C. *Soil Use Manage.* **2002**, *18*, 340–345.

54. Godfray, H. C. J.; Beddington, J. R.; Crute, I. R.; Haddad, L.; Lawrence, D.; Muir, J. F.; Pretty, J.; Robinson, S.; Thomas, S. M.; Toulmin, C. *Science* **2010**, *372*, 812–818.
55. MacLeod, M.; Moran, D.; Eory, V.; Rees, R. M.; Barnes, A.; Topp, C. F. E.; Ball, B.; Hoad, S.; Wall, E.; McVittie, A.; Pajot, G.; Matthews, R.; Smith, P.; Moxey, A. *Agric. Syst.* **2010**, *103*, 198–209.
56. Li, C. S.; Zhuang, Y. H.; Cao, M. Q.; Crill, P.; Dai, Z. H.; Frolking, S.; Moore, B.; Salas, W.; Song, W. Z.; Wang, X. K. *Nutr. Cycling Agroecosyst.* **2001**, *60*, 159–175.
57. Zhang, F.; Qi, J.; Li, F. M.; Li, C. S.; Li, C. B. *Biogeosciences* **2010**, *60*, 2039–2050.
58. Bhatia, A.; Pathak, H.; Aggarwal, P. K. *Curr. Sci.* **2004**, *87*, 317−324.
59. Roelcke, M.; Rees, R. M.; Shengxiu, L.; Richter, J. In *Soil Erosion and Dryland Farming*; Laflen, J. M., Ed.; CRC Press: Boca Raton, FL, 2000; pp 103−119.
60. Castaldi, S.; Ermice, A.; Strumia, S. *J. Biogeogr.* **2006**, *33*, 401–415.
61. Mapanda, F.; Mupini, J.; Wuta, M.; Nyamangara, J.; Rees, R. M. *Eur. J. Soil Sci.* **2010**, *61*, 721–733.
62. Stehfest, E.; Bouwman, L. *Nutr. Cycling Agroecosyst.* **2006**, *74*, 207–228.
63. Smaling, E. M. A.; Braun, A. R. *Commun. Soil Sci. Plant Anal.* **1996**, *27*, 365–386.
64. Smaling, E. M. A.; Toulmin, C. *Outlook Agric.* **2000**, *29*, 193–200.
65. Snyder, C. S.; Bruulsema, T. W.; Jensen, T. L.; Fixen, P. E. *Agric., Ecosyst. Environ.* **2009**, *133*, 247–266.
66. Gregorich, E. G.; Rochette, P.; VandenBygaart, A. J.; Angers, D. A. *Soil Tillage Res.* **2005**, *83*, 53–72.
67. Steinbach, H. S.; Alvarez, R. *J. Environ.Qual.* **2006**, *35*, 3–13.
68. van Beek, C. L.; Meerburg, B. G.; Schils, R. L. M.; Verhagen, J.; Kuikman, P. J. *Environ. Sci. Policy* **2010**, *13*, 89–96.
69. Crutzen, P. J.; Mosier, A. R.; Smith, K. A.; Winiwarter, W. *Atmos. Chem. Phys.* **2008**, *8*, 389–395.
70. Barton, L.; Kiese, R.; Gatter, D.; Butterbach-Bahl, K.; Buck, R.; Hinz, C.; Murphy, D. V. *Global Change Biol.* **2008**, *14*, 177–192.
71. Di, H. J.; Cameron, K. C. *Soil Use Manage.* **2003**, *19*, 284–290.
72. Di, H. J.; Cameron, K. C.; Sherlock, R. R.; Shen, J. P.; He, J. Z.; Winefield, C. S. *J. Soils Sediments* **2010**, *10*, 943–954.

Downloaded by CORNELL UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch014

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Chapter 15

Climate Impacts from Agricultural Emissions: Greenhouse Species and Aerosols

Jeffrey S. Gaffney,*,[1] Nancy A. Marley,[1] and John E. Frederick[2]

[1]University of Arkansas at Little Rock, 2801 S. University Avenue, Little Rock, AR 72204-1099
[2]The University of Chicago, 5734 South Ellis Avenue, Chicago, IL 60637
***E-mail: jsgaffney@ualr.edu**

Climate forcing has become a concern due to the increasing concentrations of a number of well recognized greenhouse gases in the atmosphere, such as carbon dioxide, nitrous oxide, and methane. All three of these greenhouse gases have connections to agriculture, particularly nitrous oxide and methane from rice production. However, these gases are not the only radiatively important species, as tropospheric ozone and aerosols are also important in climate change. Carbonaceous aerosols are increasing in importance, particularly as some inorganic aerosols such as sulfate are being successfully controlled. The impacts of these agriculturally important greenhouse species are overviewed here, and discussed in light of recent work using carbon isotopic measurements to examine the potential impacts of biogenic aerosols on climate. Examples from Mexico City, Chicago and Arkansas are given, which suggest that grass fires and agricultural burning can be significant sources of carbonaceous aerosols. Spectroscopic characterization of these aerosols in the UV-NIR-IR regions has clearly shown that a significantly enhanced absorption, particularly in the UV and IR, can occur from aerosols produced in agricultural and forest burning. The aerosol species responsible for this enhanced absorption has been described as "humic-like" substances (HULIS). The use of natural carbon isotope variations (^{13}C and ^{14}C) along with optical characterizations can be useful in examining the impacts of this type of burning practices,

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

especially for corn and sugar cane (C4-plants). Combustion of agricultural biowaste as a biofuel source instead of uncontrolled field burning is suggested as an alternative to current practices in the U.S.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Introduction

While some of the emission sources of the well-known greenhouse gases such as carbon dioxide, nitrous oxide, and methane are well defined and have been identified as being directly tied to specific agricultural processes, a number of other greenhouse species produced from agricultural activities are not. Ozone, which plays an important role in tropospheric air quality, is also a climate forcing greenhouse gas. Agricultural practices that involve standard field burning to remove unused debris is a major problem in the Southern, Southeastern, and Midwestern U.S. and a large source of reactive hydrocarbons and nitrogen oxide which react in the atmosphere to produce elevated ozone levels on regional scales.

Atmospheric aerosols have been identified as a major uncertainty in climate forcing due to their direct and indirect effects on radiative balance. Both scattering and absorption of radiation by aerosols are of concern in determining the impact of the aerosol direct effect. The ability of aerosols to act as cloud condensation nuclei leads to their indirect effect, as the aerosols impact both cloud formation and type. Biogenic carbonaceous aerosol sources have been found to be major contributors to both primary and secondary organic aerosols (SOA) on regional scales. Biogenic SOA are produced from the reaction of reactive biogenic hydrocarbons, emitted by both natural and agricultural vegetation, with ozone. These SOA biogenic precursors include isoprene, monoterpenes, and sesquiterpenes. Agricultural burning is also a large source of primary carbonaceous aerosols as well as reactive biogenic hydrocarbons which produce SOA.

The direct impacts of the strongly absorbing carbonaceous aerosols on climate will depend on their wavelength dependent optical properties. The degree to which atmospheric aerosols and clouds prevent the transmission of light through the atmosphere is commonly reported as the optical thickness, also known as optical extinction or atmospheric turbidity. The wavelength dependence of atmospheric extinction is traditionally described by Ångstrom's turbidity formula as $\tau = \beta \bullet \lambda^{-\alpha}$, where β, known as the Ångstrom turbidity coefficient, is the value of τ at a wavelength of 1 μm and α, known as the Ångstrom exponent, represents the wavelength dependence of the optical extinction. The total atmospheric extinction is the sum of scattering, which produces a cooling effect, and absorption, which produces a local warming effect, as $\tau = \beta_s \bullet \lambda^{-\alpha_s} + \beta_a \bullet \lambda^{-\alpha_a}$, where α_s is the Ångstrom exponent for aerosol scattering and α_a is the Ångstrom exponent for aerosol absorption. The values of the aerosol α_a give a measure of their wavelength dependent absorption profiles and their ability to cause local heating of the atmosphere. In addition, since the value of α_a is dependent on the chemical composition of the absorbing aerosol, it can serve as an indication of the type of absorbing aerosol present (*1*).

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Past work assumed that the dominant light absorbing aerosol species was carbonaceous soot produced from incomplete combustion of fossil fuel. Carbon soot is a broad band absorber with an absorption strength that decreases monotonically with wavelength (1/λ) yielding an α_a of 1 (*2*, *3*). Recently, other important light absorbing species have been observed in atmospheric aerosols including the water soluble polycarboxylic acids known as "humic-like" substances, or HULIS (*4*). Aerosol HULIS can be produced directly from biomass burning (*5*) or by atmospheric oxidation of biogenic hydrocarbons (*6*) and are therefore biogenic in nature. They can comprise up to 50% of the water soluble organic aerosol species at both urban and rural sites (*7*). Like the aquatic humic acids they are named for, HULIS contain polycarboxylic acid groups along with other unsaturated sites in an extended conjugation system. This results in intense absorbances below 400 nm, (*8*) which cause the HULIS to be yellow to brown in color leading to their being referred to as "brown carbon" (*5*, *9*). This enhanced shortwave absorption gives the aerosols containing HULIS α_a values that are greater than 1. Pure HULIS materials isolated from biomass burning aerosols have very high α_a values in the range of 6 – 7 (*5*). Mixed atmospheric aerosols produced from biomass burning have intermediate values for the α_a values of about 2-3 (*5*, *10*).

A number of laboratory studies have been conducted under controlled conditions of wildland and other biofuels and the aerosols produced characterized for their organic content and optical properties (*11–14*). These studies have also been used to estimate emission factors for the light absorbing aerosols species (*15*, *16*). These biomass derived aerosols have been observed to be wide spread having been characterized in Europe, Asia, and in the Americas (*17–22*). Studies in Mexico City serve as an example of the type of results seen in a megacity plume (*23*, *24*).

Atmospheric aerosol α_a values measured in Mexico City were observed to increase in the afternoon over the values measured in the morning (*24*). This was attributed to the photochemical formation of highly absorbing SOA in the afternoon. The α_a values were also observed to increase during periods of biomass burning. Local grass fires resulted in α_a values around 2-3 (*25*), while aged biomass burning aerosols transported long distances from the Yucatan resulted in α_a values of 1.6 (*24*). Measurements of aerosol carboxylic acid content by FTIR spectroscopy coupled with carbon isotopic analysis indicated that the enhanced α_a values observed were due to increased HULIS content of the aerosols (*26*, *27*). These results clearly indicate that there is a significant impact from biomass derived carbonaceous aerosol sources even in the large urban area of Mexico City and that these aerosols have absorption profiles that are enhanced in the shortwave region over those derived from fossil fuel combustion. This enhanced shortwave absorption can lead to local heating of the atmosphere and changes in climate and weather patterns.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Carbon Isotopic Measurements

The measurement of radiocarbon (^{14}C) in atmospheric aerosol samples can give a measure of the amounts of aerosol carbon produced from fossil fuel and non-fossil fuel sources. All biogenic materials are labeled with a relatively constant initial $^{14}C/^{12}C$ ratio (*28*). Aerosols produced from the combustion of this biogenic material will have the same ^{14}C content as the source material. The aerosols produced from the combustion of fossil fuels contain no ^{14}C because the age of the fuel is much greater than the 5730-year half-life of the ^{14}C. Therefore, the ^{14}C content in atmospheric aerosols, reported as the fraction of modern carbon, provides a direct measure of the relative contributions of carbonaceous materials derived from fossil fuels and that derived from modern biomass sources. The ^{14}C content of atmospheric aerosols determined in samples collected in a number of areas are summarized in Table I.

Early measurements made in Barrow, AK (*29*), Los Angeles (*30*) and Denver (*31*) previous to the year 2000 showed a lower modern carbon content than those made later reflecting a higher percentage of fossil fuel derived aerosols during that time (*30*, *31*). Later measurements have resulted in larger modern carbon fractions reflecting a lower percentage of fossil-derived carbon in atmospheric aerosols. This is possibly a result of implementing tighter emission controls on motor vehicle emissions from fossil fuels, the growing use of biofuels, and little or no control of open biomass and trash burning in many areas (*32*).

The high levels of modern carbon reported in Table I for Launceston, Tasmania were attributed to high levels of residential wood burning in the wintertime (*33*). The high modern carbon levels observed in Nashville (*34*), Tampa (*35*), and the park sites of Yosemite, Brigantine National Wildlife Refuge (BNW), Mt. Rainier, Rocky Mountain National Park, and Tonto National Monument (TNM) (*36*) were attributed to biogenic SOA formation. The very high values for fraction modern carbon (> 1.0) observed in some rural areas may have been due to contributions from the burning of older trees which contained "bomb carbon" from nuclear testing in the 1950s resulting in $^{14}C/^{12}C$ ratios higher than seen in modern biomass.

The modern carbon aerosol content observed at Tecamac, a suburban, rural site located 18 miles north of Mexico City, was higher than that observed in the city due to impacts from local grass fires. The biogenic impacts in this area were observed to be as high as 90% (*37*, *38*).

The fraction of modern carbon was determined in the organic carbon (OC) and elemental carbon (EC) aerosol fractions in Mexico City by using thermal evolution methodologies described previously (*39–47*).

The results shown in Figure 1 indicate that the EC fraction, which is made up of the high molecular weight soots generated by incomplete combustion, contain less modern carbon than the smaller molecular weight OC fractions while the results for the total aerosol carbon are generally shown to be midway beween the EC and OC values. Similar results have been reported in studies in Okinawa, Japan where the black carbon (BC) aerosol component was found to be 67% modern compared to 94% modern in the OC fraction (*48*).

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table I. The fraction of modern carbon in atmospheric aerosols reported for some urban areas

Location	*Year*	*Modern C*		*Reference*
		Range	*Average*	
Barrow, AK	1982	0.42-0.46	0.4	(*29*)
Long Island, NY	1982	0.37-0.40	0.4	(*29*)
Los Angeles, CA	1982	0.20-0.43	0.3	(*30*)
Denver, CO	1996-97	0.05-0.69	0.3	(*31*)
Nashville, TN	1999	0.56-0.80	0.7	(*34*)
Houston, TX	2000	0.27-0.77	0.5	(*39*, *40*)
Look Rock, TN	2000-01	0.54-0.83	0.7	(*41*)
Tampa, FL	2002	0.55-0.95	0.7	(*35*)
Zurich,CH	2002	0.60-0.67	0.6	(*42*)
Yosemite, CA	2002	0.80-1.05	0.9	(*43*)
Tokyo, JP	2002-04	0.31-0.52	0.4	(*44*)
Aveiro, PT	2002-04	0.77-0.92	0.8	(*45*)
Puy de Dôme, FR	2002-04	0.72-0.87	0.8	(*45*)
Schauinsland, DE	2002-04	0.79-0.84	0.8	(*45*)
Mexico City, MX	2003	0.56-0.86	0.7	(*25*)
Launceston, AU	2003-04	0.96-1.11	0.9	(*33*)
Seattle, WA	2004-05	0.38-0.69	0.6	(*36*)
BNW, NJ	2004-05	0.30-0.99	0.8	(*36*)
Mt. Rainier, WA	2004-05	0.75-1.10	0.9	(*36*)
Tokyo, JP	2004-05	0.31-0.54	0.4	(*46*)
Phoenix, AZ	2005-06	0.49-0.75	0.6	(*36*)
Rocky Mt. NP, CO	2005-2006	0.78-1.11	1.0	(*36*)
TNM, AZ	2005-2006	0.64-1.04	0.8	(*36*)
Mexico City, MX	2006	0.42-0.75	0.6	(*25*)
Tecamac, MX	2006	0.55-0.96	0.8	(*25*)

BNW = Brigantine National Wildlife Refuge; TNM = Tonto National Monument

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

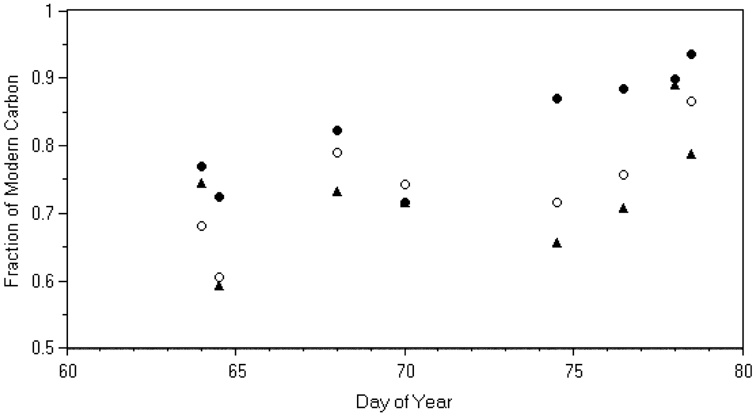


Figure 1. Fraction of modern carbon in organic carbon (•) elemental carbon (▴), and total carbon (○) fractions of aerosol samples collected in Mexico City and Tecamac in 2006.

Overall, the fraction of modern carbon in the EC aerosol component was 0.67 in Mexico City and 0.75 at Tecamac. The corresponding results for the OC component were 0.75 in Mexico city and 0.85 at Tecamac. This is consistent with input from the local grass fire sources at Tecamac and diesel soot being a major source of EC in the Mexico City urban area. In any case, data obtained in Mexico City as well as the many other areas listed in Table I suggests that the biogenic contributions to carbonaceous aerosols are becoming significant world wide and their effects on radiative balance will need to be considered in future climate modeling efforts.

Organic Reactivity and SOA

It is important to recognize that the volatile organics emitted from both fossil fuel sources and from biogenics have very different reactivities with OH, nitrate radical and ozone. A comparison of the reactivity for some common organics and natural hydrocarbons with OH is given in Table II.

In general, the alkenes are more reactive than the alkanes and aromatic hydrocarbons. This is due to the ability of OH radicals to add to the olefinic double bond. Another trend is that the presence of functional groups that donate electrons to the double bond increases the reactivity. Thus, larger alkenes react faster than smaller ones. Alkanes react with OH by abstraction and those with more secondary and tertiary protons will be more reactive. Therefore, as with the alkenes, larger alkanes will react faster. Oxidized organics are typically less reactive with OH, as in most cases they react by abstraction and therefore their reactivities are comparable to the small alkanes. The ozone and nitrate radical reactivities for these hydrocarbons also follow the same general trend as the OH reactivities as they are all electrophilic reagents.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Table II. Reaction rates of some important volatile hydrocarbons with OH (*36*)

Hydrocarbon	*rate x 10 ^{12} cm^3 molecule^{-1} s^{-1}*
Alkenes	
Ethene	8.5
Propene	26
1-butene	31
1-pentene	31
1-hexene	37
cis-2-butene	56
trans-2-butene	67
2-methyl-2-butene	87
2,3-dimethyl-2-butene	110
2-methylpropene	51
Cyclohexene	68
1,3-butadiene	67
2-methyl-1,3-butadiene (isoprene)	101
Limonene	171
beta-caryophyllene	collisional
Alkanes	
Ethane	0.03
n-Butane	2.5
Cyclohexane	7.4
Others	
Acetylene	0.08
Benzene	1.3

Since emissions from fossil fuel sources have been identified as “anthropogenic” pollutants, we have implemented control strategies for the volatile organics emitted from both mobile and stationary sources in order to reduce ozone formation in urban areas. One important control strategy is the use of catalytic converters for mobile sources. This same reactivity trends listed in Table II also occur in catalytic oxidation. Thus, in catalytic converters the more reactive alkenes and larger alkanes are most effectively removed yielding emissions primarily composed of the much less reactive hydrocarbons. With time, these measures have led to the reduction of the most reactive anthropogenic volatile organic compounds (VOCs) and to a reduction in the overall reactivity of the emissions. While the organic reactivity of the emissions from motor

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

vehicles and energy related stationary sources has been reduced, the nitrogen oxide emissions have not been lowered. Thus, the result of this reduction in anthropogenic VOC reactivity has led to a slower production of ozone and a transition from the formation of high ozone levels in urban areas to elevated ozone concentrations on regional scales.

Note in Table II that the biogenic hydrocarbons isoprene, d-limonene and beta-caryophyllene are extremely reactive compared to the anthropogenic hydrocarbons. The biogenic hydrocarbons, isoprene (C5 hemiterpene), the monoterpenes (C10), and especially the sesquiterpenes (C15) have atmospheric lifetimes typically of minutes to hours in urban environments and hours to days in regional areas. The less reactive anthropogenic organic emissions tend to have lifetimes on the order of hours to days in urban environments, and days to months on regional scales (*49*). Unless they are photochemically reactive, the oxidized organic hydrocarbons have atmospheric lifetimes that are are typically much longer. For comparison, at a OH radical concentration of 1.0 x 10^6 molecules per cc, typical of an urban environment, the lifetime of ethane is 43 days, ethene is 1.4 days, and cis-2-butene is 5 hours, while the biogenic hydrocarbons have lifetimes of minutes to hours. Indeed, the sesquiterpenes are so reactive with OH and ozone that they are typically very difficult to measure directly in the atmosphere and have to be inferred from measurements of their reaction products.

These very reactive biogenic hydrocarbons are emitted from living vegetation including natural as well as anthropogenically managed agricultural areas. The estimated total emission rate in the U.S. is 30.7 Mt annually with more than half of these emissions occurring in summer, and approximately half in the Southeastern and Southwestern U.S (*50*). The actual fraction of land used for agricultural purposes in the Midwestern, Southern, and Southeastern U.S. is considerable as compared to land left in the “natural state”. While the percentage of cropland in the U.S., excluding Alaska, was approximately 23% in 2002 (*51*), this fraction approaches or exceeds 40-50% in many portions of the midwest and south.

As we increase controls on the VOC emissions from fossil fuel sources, and the overall hydrocarbon emission reactivity from these sources is lowered, ozone formation rates as well as the SOA formation rates from these sources are lowered. At the same time the nitrogen oxide emissions have not been controlled and the atmospheric levels remain high so that ozone levels are increasing regionally. This has the effect of increasing the ozone reactions with the very reactive biogenic hydrocarbons and increasing the formation rates of the biogenic SOA reaction products. This expected increase in biogenic SOA is a contributing factor to the observed increases in the fraction of modern carbon observed in carbonaceous aerosols over the years.

Primary Combustion Aerosols

Carbonaceous aerosols from leaf burning and regional agricultural burning practices are a substantial source of carbonaceous aerosols in the Southern U.S., with Arkansas, Louisiana, and Florida contributing more than 75% of all agricultural burning in the southeast (*52*). In 2004, results from the Moderate

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Resolution Imaging Spectroradiometer (MODIS) satellite data showed that 73% of all the fire activity in Arkansas was due to agricultural burning with the highest activities occurring in June and October – January (*52*). As part of an effort to evaluate the aerosol optical properties in this region, a number of instruments have been operated at the Chemistry Department of the University of Arkansas at Little Rock (UALR), Little Rock, AR. These included a 7-wavelength aethalometer to measure aerosol absorption, aerosol α_a, and BC aerosol levels. The instrumentation and methods used have been described previously in detail (*24*, *25*).

Figure 2 shows the BC concentrations measured at UALR from October to December, 2010 compared to measurements made by the same methods at The University of Chicago (U of C) from October to December, 2007. During this time period the biogenic VOC emissions would be minimal in both areas decreasing the input from SOA formation. The observed BC would therefore be primarily from fossil fuel or biogenic combustion. The BC levels observed at The U of C were significantly lower than at UALR by a factor of 2-3. The overall average in Chicago during this period was 0.4 μg/m^3 compared to 0.8 μg/m^3 at UALR and the maximum levels observed were 2.8 μg/m^3 in Chicago and 7.9 μg/m^3 in Little Rock.

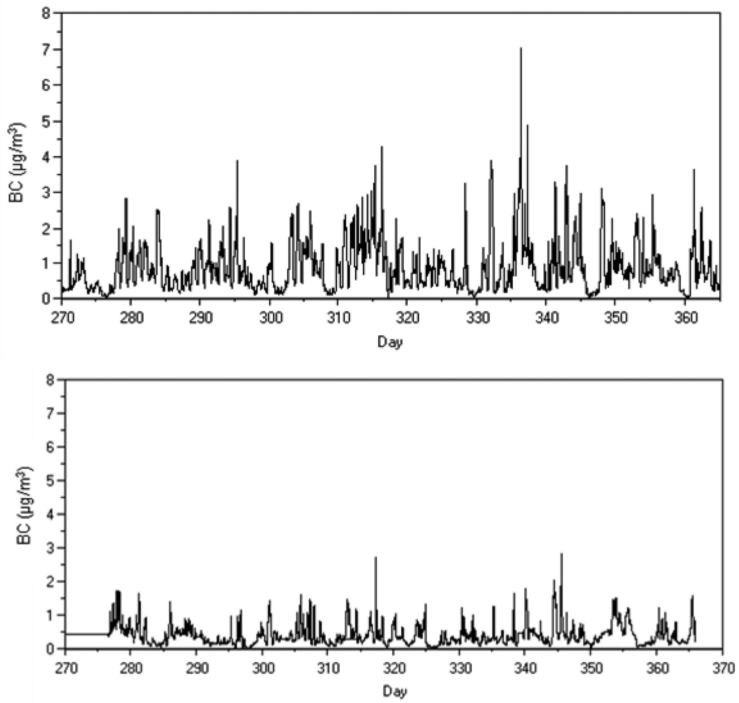


Figure 2. Black carbon (BC) levels measured at the University of Arkansas at Little Rock (top) and at The University of Chicago (bottom) from October to December 2010 (UALR) and 2007 (U of C).

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

The site at the U of C was located in Southside Chicago and highly impacted by diesel truck traffic from the nearby expressways as well as campus traffic, while the site in Little Rock was located on the heavily wooded UALR campus in Southwestern Little Rock and not heavily impacted by local traffic. The only source of biomass combustion in Chicago would be wood burning fireplaces, which are minimal in the immediate area. However, there are no open burning controls in Arkansas and leaf and trash burning as well as agricultural burning are common during this time period. The higher BC levels observed in Little Rock would therefore indicate a significantly higher level of combustion aerosols in Little Rock compared to the large urban area of Chicago. Note the population of Little Rock is approximately 190,000 as compared to Chicago's population of 2.85 million.

It should also be noted that in addition to the production of high levels of carbonaceous aerosols, the open burning practices common in the Southern U.S. also produce regional ozone from nitrogen oxide and reactive organic emissions released during combustion. Ozone is a regulated atmospheric pollutant and a recognized human health hazard as well as a greenhouse gas. In addition, open burning also produces significant amounts of carbon monoxide and aldehydes. Aldehydes (e.g. formaldehyde, acetaldehyde, acrolein, crotonaldehyde, etc.) are considered air toxics and have immediate high level eye-irritation or lachyrmator potential along with long term carcinogenic exposure potential to downwind populations.

Natural Isotopic Labeling To Assess Agricultural Burning Sources

The natural labeling of vegetation with different ratios of stable carbon isotopes ($^{13}C/^{12}C$) due to their different photochemical pathways can also help to identify the biomass aerosol sources. The C-3 plants, which utilize the Calvin-Benson photosynthetic cycle, have a more selective chemistry and fractionate the heavier carbon isotope (^{13}C) by about 12-14 parts per thousand as compared to the less selective C-4 or Hatch-Slack photosynthetic pathway. The C-3 and C-4 plants will therefore be labeled with different $^{13}C/^{12}C$ ratios. The C-3 plants are most abundant and comprise most tree species, shrubs, and cool temperate grasses and sedges, while the C-4 plants consist mostly of warm temperate to tropical grasses (*53*). The $^{13}C/^{12}C$ ratios are commonly expressed as $\delta^{13}C$ values in per-mil (‰), and represent the difference between the measured ratios and that of a carbon isotope standard, typically CO_2 prepared from Peedee belemnite carbonate. The measured $^{13}C/^{12}C$ ratios of organic matter are generally ^{13}C-depleted compared to that of the standard and are therefore reported as negative values. These resulting $\delta^{13}C$ values can be used to estimate the relative contributions from C-3 ($\delta^{13}C = -27 \pm 6$) and C-4 ($\delta^{13}C = -13 \pm 4$) plant sources to the carbonaceous aerosols.

Taken together with ^{14}C measurements these determinations can allow for the impacts from specific agricultural burning activities to be assessed. A comparison of the ^{13}C ratios with the fraction of modern carbon is shown in Figure 3 for fine aerosols collected in Mexico City and Tecamac in 2006 (*25*, *37*). The results of

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

-25 ‰ $\delta^{13}C$ and near the 100 % fraction modern carbon observed at Tecamac are indicative of aerosols produced from the combustion of biomass composed of both C-3 and C-4 grasses. The results shown for the Mexico City aerosols are typical of fossil fuel combustion mixed with biomass burning aerosols. Mexico City was impacted both by grass fires to the north and widespread forrest fires in the Yuccatan during this period (*54*, *55*).

The values expected from carbonaceous aerosols produced from the combustion of different sources are also shown in Figure 3. For instance, the practice of burning sugar cane debris (C4 plant) in the Southern U.S. will lead to the release of carbonaceous soot aerosols and reactive aldehydes enriched in ^{13}C and ^{14}C content (-12 ‰ $\delta^{13}C$ and a 100% fraction modern C). This is contrasted with that expected from the combustion of wood (C3 plant) producing aerosols more depleted in ^{13}C (-25 ‰ $\delta^{13}C$ and 100% fraction modern carbon) and that from fossil fuel combustion yielding aerosols depleted in both ^{13}C and ^{14}C (-25 ‰ $\delta^{13}C$ and 0% fraction modern). Therefore, measurements of the carbon isotopic content of the fine aerosols produced during a burning event of sugarcane debris from agricultural fields will give isotopic signitures that are distinct from that produced from these other sources, as represented in Figure 3.

The integrated nature of the carbon isotopic measurements also allows for the actual mass fraction of aerosols produced from combustion of different materials to be assessed during these events. Similarly, the use of carbon isotopes can be combined with other tracers of opportunity such as fine potassium or halogen content to assess the impacts from other types of agricultural burn events. These methods have recently been applied to aid in source determination for long range transported aerosols impacting the pacific northwest (*56*).

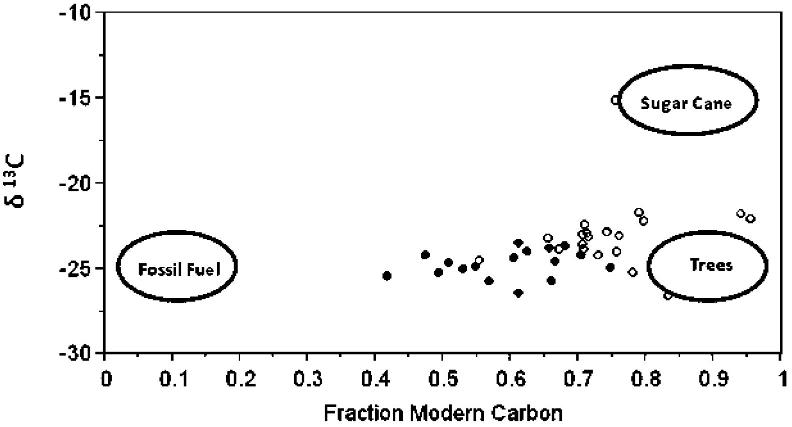


Figure 3. Carbon isotopic ratios of fine aerosols in Mexico City (•) and Tecamac (○) in 2006. Results expected from the combustion of fossil fuel, sugar cane, and trees and grasses are indicated with ovals.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Alternative Uses for Biomass

Agricultural field stubble removal by open combustion processes currently in use is not necessarily the best option when considering the potential impacts on regional ozone production from nitrogen oxide and reactive organic emissions as well as the climate impacts from released greenhouse gases and carbonaceous aerosols associated with these burning events. Alternate approaches to disposing of these unused materials should be considered. One option is the potential use of this agricultural debris as a direct biofuel replacement for coal as a cleaner energy source. A simple comparison of the energy content of the different types of agricultural materials and wood debris to coal and oil used for power plant fuels is given in Table III (*57*).

The data shown in Table III indicate the potential energy content in these unused agricultural residues. This is a potentially renewable fuel source which should not be neglected. While the use of this material to produce alcohols, biodiesel, and other liquid fuels is being explored, the direct, controlled, high temperature combustion of dried agricultural carbon residues from crops should be considered where open field burning is common. In this case, controlled combustion of these materials as an alternative to open burning could lead to the reduction of greenhouse species as well as to reduce the agricultural impacts on regional ozone formation while providing an alternative source of energy. This would help to obtain a sustainable energy situation for agriculture. The agricultural (Ag) residues listed in Table III include sugar cane bagasse, rice straw, and wheat and corn stover. It should be noted that the energy content listed for ethanol and biodiesel is for the final product and does not take into account the energy costs to produce the final liquid fuel.

Organics in Precipitation

Precipitation samples were collected at UALR on the roof-top of the Science Lab Building during 2009, 2010, and 2011 using an automated wet-dry sample collector. The total dissolved organic carbon (DOC) was measured in each rain sample using a Shimadzu DOC analyzer. Figure 4 shows the total amount of rain recorded at the site and the DOC in each rain sample after filtration through a 0.45 membrane filter to remove suspended particulates.

The DOC levels were observed to increase beginning in May (day 140) and continue through August (day 245). The average DOC observed during this time period was 4 ppm with a maximum of 8.5 ppm in June. Note that this is peak time for both biogenic emissions and agricultural burning activities (*47*, *52*). Analysis of the rain samples using mass spectrometry found that the water soluble organics present in the samples are less than 500 daltons molecular weight (*58*). This is also consistant with results found on aerosol HULIS (*59*). The area near Little Rock is heavily forested with deciduous (isoprene emitting) and coniferous (monoterpene emitting) trees. A comparison of the reaction products of ozone with beta-caryophyllene have found them to be of similar molecular weight. These results suggest that a significant amount of the dissolved organics in the rainfall may be due to low molecular weight oxidation products of biogenic hydrocarbons. However, it should also be noted that the organics produced from open burning will likely be a mix of oxidized compounds that will be of similar structure to those produced from the low temperature atmospheric oxidations by OH radical and other oxidants in the troposphere.

There are very few measurements of ^{14}C in DOC in rainwater. However, the few that have been reported in coastal North Carolina have found the DOC to contain 76-96 % modern carbon (*60*). This is again consistent with a biomass source for the soluble organic compounds in the rainwater. The input of this biogenic DOC from rainwater into surface waters can be important on regional scales. For example, the flux of these oxidized organics into Lake Maumelle, a Little Rock drinking water source, is estimated to be approximately one ton of carbon per average rain event.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

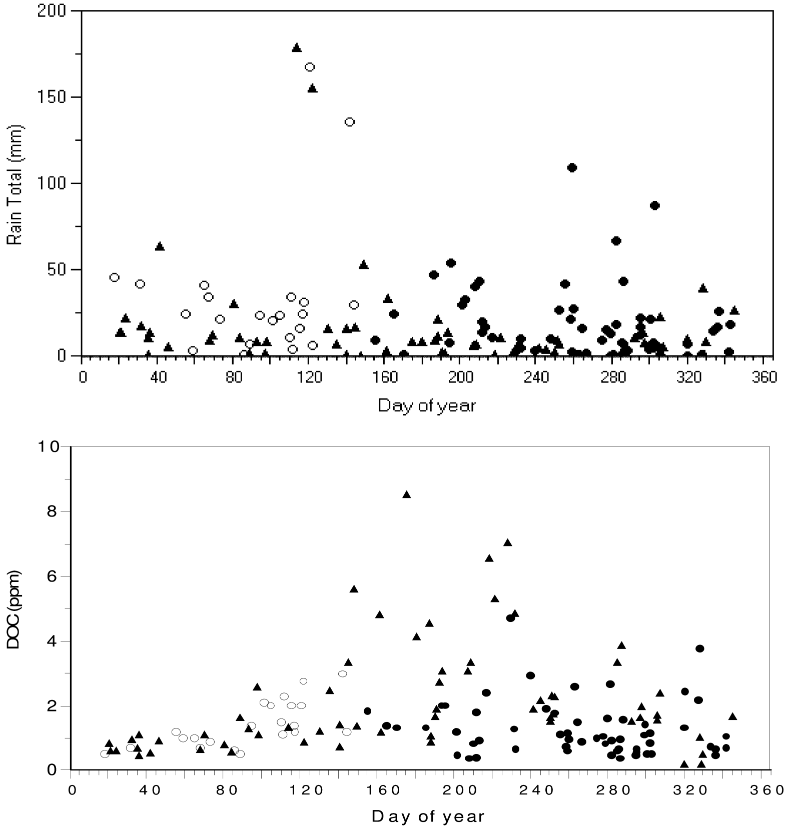


Figure 4. Total amount of rain (top) and dissolved organic carbon (DOC) concentration (bottom) in rainwater samples collected at UALR in 2009 (•) and 2010 (▲) and 2011 (○).

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Table III. Energy content in gigajoules per metric tone (GJ/T) of some biomass and fossil fuels

Carbonaceous Fuel Source	*Energy Content (GJ/T)*
Biomass	
Dry Wood	18-22
Wet Wood – (20% moisture content)	15
Ag residues – Wet	10-17
Charcoal (from 90-180 GJ original wood content)	30
Ethanol	26.7
Biodiesel	37.8
Fossil	
Gasoline	47.3
Diesel –	42.8
Coal − anthracite	27-30
Coal – bituminous	27
Lignite	15-19

The BC concentrations and the aerosol α_a determined from a 7 wavelength aethalometer as described previously (*24*) are shown in Figure 5 along with total rain amounts measured at the UALR site from August to December 2010. Examination of the data shows that there is significant amounts of carbon that remain in the atmosphere during rain events. However, the aerosol α_a are closer to a value of 1 during and immediately following significant rain events. An α_a of 0.9 to 1.0 is typical for diesel soot, while α_a higher than 1.0 indicate the presence of UV absorbing compounds such as HULIS that are produced from biogenic VOC reactions with OH and ozone or from biomass burning (*25*).

This indicates that the rain preferentially removes the water soluble aerosol components with enhanced shortwave absorption, typical of HULIS, leaving behind the more hydrophobic BC. It is likely this occurs due to partitioning of semi-volatiles between the surfaces of aerosols and cloud water droplets thus allowing for the removal of the oxidized organics through wet deposition accompanied by the observed lowering of the absorption exponents to the base diesel soot values during rain events.

A significant amount of the carbonaceous aerosols in the submicron region is not removed during the rain events and this will lead to longer lifetimes for these more hydrophobic species. It also indicates that the remaining BC would be transported over much longer distances than the oxidized reaction products which are more readily removed from the atmosphere by wet deposition. These results show that not only the aqueous and solid phase equilibria need to be considered in determining the distribution of carbonaceous aerosol species but the gas-liquid partitioning of the semi-volatile organics present in the aerosols also need to be included. Thus, Henry's law coefficients for many of the partially oxidized organic species need to be determined in future work

Climate Impacts of Biogenic Aerosols

Measurements of the mass absorption coefficient (B_a) of the atmospheric carbonaceous aerosols in Mexico City have been reported as 10.9±2.1 m^2/g at 660 nm (*61*). The wavelength dependent absorption profiles from 290 to 600 nm for a diesel soot type BC aerosol with this absorption strength and an α_a value of 1 is shown in Figure 6 compared to the wavelength dependent absorption profile for a mixed fossil fuel plus biomass burning type aerosol with an α_a of 1.6, as measured in Mexico City previously (*24*).

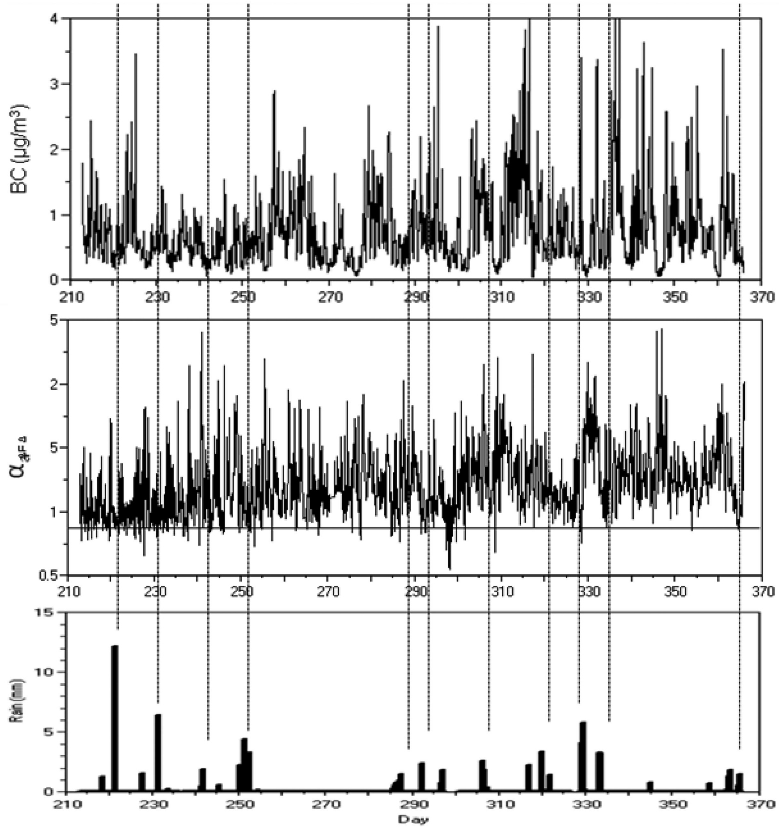


Figure 5. Black carbon concentrations (top), Ångstrom exponents for aerosol absorption (middle), and total rain amount (bottom) measured at UALR during August-December, 2010. Major rain events are indicated by vertical lines.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

In order to estimate the atmospheric heating potential of the BC aerosols shown in Figure 6, the relative energy absorbed can be calculated from the wavelength dependent solar irradiance at ground level (Figure 7A).

Note that the irradiance at ground level is reduced from that anticipated at the top of the atmosphere due to absorption by atmospheric gases. For example, absorption by stratospheric ozone removes a significant amount of short-wave radiation in the 280-300 nm wavelength range preventing it from reaching ground level. It should also be noted that while the number of photons reaching the ground in the UVB and UVA regions is significantly lower than that expected at 550 nm, there is significant energy associated with these photons and thus the ground level irradiance (W/cm^2-μm) peaks at around 450 nm.

The relative amounts of energy absorbed by equal amounts of the two types of BC aerosols in Figure 6 can be obtained by multiplying the solar irradiance (Figure 7A) by the wavelength dependent B_a of the two types of BC aerosols (Figure 6). The result shown in Figure 7B demonstrates that the biomass type aerosol absorbs approximately 1.5 times more energy than the soot type aerosol at the irradiance peak of 450 nm and 1.7 times more energy in the UVA region (350 nm). An integration of the energy curves from 290 to 600 nm yields a total absorption ratio in the UV-visible region of 1.46 to 1 for the biomass to the diesel soot type aerosols, indicating that the biomass type BC would trap 46 % more energy in the lower atmosphere than the same amount of diesel soot type BC aerosols due to their enhanced shortwave absorption. This clearly shows the potential for biomass burning BC aerosols containing HULIS as well as similar oxidized compounds found in biogenic SOA to impact energy absorption in the region of 290-600 nm.

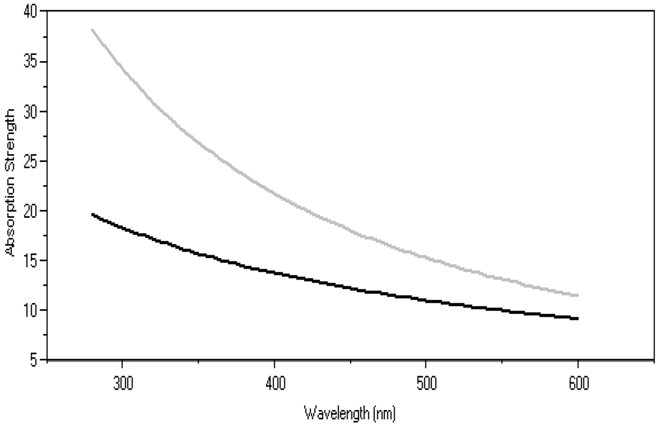


Figure 6. Absorption strengths (m^2/g) for a soot type BC aerosol (▬) and a biomass type BC aerosol (▬).

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

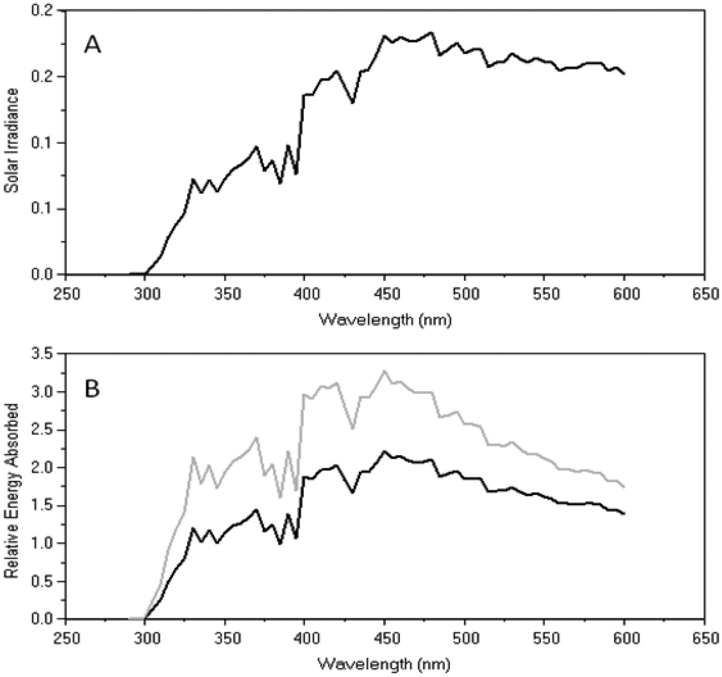


Figure 7. A) Solar irradiance at ground level (W/cm^2-μm). B) relative energy absorbed by a soot type BC aerosol (▬) and a biomass type BC aerosol (▬) present in the lower atmosphere (units of watts per micron per gram carbonaceous aerosol x 10).

Conclusions

In assessing the impacts of agricultural practices on climate, the current focus is on carbon dioxide as the major greenhouse species, although some attention is now being given to methane and nitrous oxide, particularly in rice production where anaerobic bacterial emissons of these gases can be significant during flooding. However, there is currently significant evidence that agricultural burning practices are leading to the uncontrolled releases of significant levels of nitrogen oxide, reactive organics, and carbonaceous aerosols (both primary and secondary), as well as oxygenates such as aldehydes, on large scales. These emissions need to be controlled as they have significant impacts on climate as well as on regional air quality. The release of nitrogen oxide and reactive organics leads to the production of tropospheric ozone, a regulated air pollutant and greenhouse gas. Carbonaceous aerosols that absorb in the UV – Visible regions, will add to regional heating and changes in local climate and weather. These same organics are water soluble and removed by rainfall events which adds to the organic loadings in surface waters.

In addition, climate change may lead to enhanced production of absorbing carbonaceous aerosols and biogenic SOA produced from the oxidations of isoprene, monoterpenes, and sesquiterpene emissions from deciduous and pine forests. While forest fires and biogenic hydrocarbon emissions are natural processes, they are likely to be impacted indirectly by anthropogenic factors. These include increases in carbon dioxide that act to "fertilize" plant growth and climate warming and precipitation changes that are known to lead to enhanced emissions of biogenic hydrocarbons, as well as earlier springs and longer growing seasons that lead to increases in brush and forest fires. This all serves to increase production of both primary and secondary biogenic aerosols, which have UV and IR absorptions that may impact radiation balance on regional scales.

While the current practices of agricultural combustion are continuing, particularly in the Southeastern and Midwestern U.S., serious consideration should be placed on developing alternative uses of these waste materials. In particular, the potential use of agricultural waste as an alternate fuel for power plant operation should be considered. This would lead to a more sustainable energy source and would be a means of controlling one environmental problem while producing a source of cleaner energy than the combustion of coal.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Acknowledgments

This work was conducted as part of the Department of Energy's Atmospheric Systems Research. This research was supported by the Office of Science (BER), U.S. Department of Energy Grant No. DE-FG02-07ER64329. Dr. Tom Guilderson of the Center for Accellerator Mass Spectrometry and Dr. Neil Sturchio of the University of Illinois at Chicago are also thanked for assistance in obtaining carbon isotope data noted in this work. Ms. Gail Bridges is acknowledged for collecting precipitation samples and performing DOC analyses.

References

1. Bergstrom, R. W.; Pilewskie, P.; Russell, P. B.; Redemann, J.; Bond, T.; Quinn, P. K.; Sierau, B. *Atmos. Chem. Phys.* **2007**, *7*, 5937–5943.
2. Bergstrom, R. W.; Russell, P. B.; Hignett, P. B. *J. Atmos. Sci.* **2002**, *59*, 567–577.
3. Marley, N. A.; Gaffney, J. S.; Baird, J. C.; Blazer, C. A.; Drayton, P. J.; Frederick, J. E. *Aerosol Sci. Technol.* **2001**, *34*, 535–549.
4. Cappiello, A.; De Simoni, E.; Fiorucci, C.; Mangani, F.; Palma, P.; Trufelli, H.; Decesari, S.; Facchini, M. C.; Fuzzi, S. *Environ. Sci. Technol.* **2003**, *37*, 1229–1240.
5. Hoffer, A.; Gelencer, A.; Guyon, P.; Kiss, G.; Schmid, O.; Frank, G. P.; Artaxo, P.; Andreae, M. O. *Atmos. Chem. Phys.* **2006**, *6*, 3563–3570.
6. Iinuma, Y.; Muller, C.; Boge, O.; Gnauk, T.; Herrmann, H. *Atmos. Environ.* **2007**, *41*, 5571–5583.
7. Limbeck, A.; Kulmala, M.; Puxbaum, H. *Geophys. Res. Lett.* **2003**, *30*, doi:10.1029/2003GL017738.

8. Gaffney, J. S.; Marley, N. A.; Clark, S. B. In *Humic and Fulvic Acids, Isolation, Structure, and Environmental Role*; Gaffney, J. S., Marley, N. A., Clark, S. B., Eds.; : Washington, DC, 1996; Chapter 1, pp 2−16.
9. Andreae, M. O.; Geleneser, A. *Atmos. Chem. Phys.* **2006**, *6*, 3131–3148.
10. Kirchstetter, T. W., Novakov, T., Hobbs, P. V. *J. Geophys. Res.* **2004**, *109*, D21208, doi:10.1029/2004JD004999.
11. Chen, L.-W. A.; Moosmuller, H.; Arnott, W. P.; Chow, J. C.; Watson, J. G.; Susott, R. A.; Babbitt, R. E.; Wold, C. E.; Lincoln, E.; Hao, W. M. *Geophys. Res. Lett.* **2007**, *33*, 1–4.
12. Chen, L.-W. A.; Moosmuller, H.; Arnott, W. P.; Chow, J. C.; Watson, J. G.; Susott, R. A; Babbitt, R. E.; Wold, C. E.; Lincoln, E. N; Hao, W. M. *Environ. Sci. Technol.* **2007**, *41*, 4317–4325.
13. Day, D. E., Hand, J. L., Carrico, C. M., Engling, G., Malm, W. C. *J. Geophys. Res. Atmos.* **2006**, *111*, D22202, doi: 22210.21029/22006JD007221.
14. McMeeking, G. R.; Kreidenweis, S. M.; Baker, S.; Carrico, C. M.; Chow, J. C.; Collett, J. L.; Hao, W. M.; Holden, A. S.; Kirchstetter, T. W.; Malm, W. C.; Moosmuller, H.; Sullivan, A. P.; Wold, C. E. *J. Geophys. Res. Atmos.* **2009**, *114*, doi:10.1029/2009JD011836.
15. Sandradewi, J.; Prevot, A. S. H.; Weingartner, E.; Schmidhauser, R.; Gysel, M.; Baltensperger, U. *Environ. Sci. Technol.* **2008**, *42*, 3316–3323.
16. Chow, J. C.; Watson, J. G.; Lowenthal, D. H.; Chen, L.-W. A.; Motallebi, N. *J. Air Waste Manage. Assoc.* **2010**, *60*, 497–507.
17. Chakrabarty, R. K.; Moosmuller, H.; Chen, L.-W. A.; Lewis, K.; Arnott, W. P.; Mazzoleni, C.; Dubey, M. K.; Wold, C. E.; Hao, W. M.; Kreidenweis, S. M. *Atmos. Chem. Phys.* **2010**, *10*, 6363–6370.
18. Sandradewi, J.; Prevot, A. S. H.; Weingartner, E.; Schmidhauser, R.; Gysel, M.; Baltensperger, U. *Atmos. Environ.* **2008**, *42*, 101–112.
19. Favez, O.; Cachier, H.; Sciare, J.; Sarda-Esteve, R.; Martinon, L. *Atmos. Environ.* **2009**, *43*, 3640–3644.
20. Favez, O.; El Haddad, I.; Piot, C.; Boreave, A.; Abidi, E.; Marchand, N.; Jaffrezo, J. L.; Besombes, J. L.; Personnaz, M. B.; Sciare, J.; Wortham, H.; George, C.; D'Anna, B. *Atmos. Chem. Phys.* **2010**, *10*, 5295–5314.
21. Jung, J.; Kim, Y. J.; Lee, K. Y.; Cayetano, M. G.; Batmunkh, T.; Koo, J. H.; Kim, J. *Atmos. Chem. Phys.* **2010**, *10*, 5391–5408.
22. Zhang, X. Y.; Wang, Y. Q.; Xhang, X. C.; Guo, W.; Niu, T.; Gong, S. L.; Yin, Y.; Zhao, P.; Jin, J. L.; Yu, M. *Tellus, Ser.* **2008**, *60*, 647–656.
23. Molina, L. T.; Madronich, S.; Gaffney, J. S.; Apel, E.; de Foy, B.; Fast, J.; Ferrare, R.; Herndon, S.; Jimenez, J. L.; Lamb, B.; Osornio-Vargas, A. R.; Russell, P.; Schauer, J. J.; Stevens, P. S.; Volkamer, R.; Zavala, M. *Atmos. Chem. Phys.* **2010**, *10*, 1–64.
24. Marley, N. A.; Gaffney, J. S.; Castro, T.; Salcido, A.; Frederick, J. *Atmos. Chem. Phys.* **2009**, *9*, 189–206.
25. Marley, N. A.; Gaffney, J. S.; Tackett, M.; Sturchio, N. C.; Heraty, L.; Martinez, N.; Hardy, K. D.; Marchany-Rivera, A.; Guilderson, T.; MacMillan, A.; Steelman, K. *Atmos. Chem. Phys.* **2009**, *9*, 1537–1549.
26. Marley, N. A.; Gaffney, J. S.; Kelley, K. L.; Sarkar, A.; Bridges, G. L. *Eos Trans. AGU Fall Meet. Suppl.* **2009**, *90*, A13C–0241.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

27. Gaffney J. S.; Marley, N. A. 89th National Meeting of the American Meteorological Society. *Tenth Conference on Atmospheric Chemistry, Conference Proceedings Volume*; 2009, Paper J1.1, 4.
28. Currie, L. A.; Klouda, G. A.; Gerlach, R. W. In *Proceedings of the 1981 International Conference on Residential Solid Fuels: Environmental Impacts and Solutions*; Cooper, J. A., Malek, D., Eds.; Oregon Graduate Center: Beaverton, OR, 1982; pp 365−385.
29. Gaffney, J. S.; Tanner, R. L.; Phillips, M. *Sci. Total Environ.* **1984**, *36*, 53–60.
30. Hildemann, L. M.; Klinedinst, D. B.; Klouda, G. A.; Currie, L. A.; Cass, G. R. *Environ. Sci. Technol.* **1994**, *28*, 1565–1576.
31. Klinedinst, D. B.; Currie, L. A. *Environ. Sci. Technol.* **1999**, *33*, 4146–4154.
32. Gaffney, J. S.; Marley, N. A. In *Air Pollution Reviews: Volume 1, Alternate Fuels*; Brimblecombe, P., Maynard, R., Eds.; Imperial College Press: London, U.K., 2000; Chapter 6, pp 195−246.
33. Jordan, T. B.; Seen, A. J.; Jacobson, G. E.; Gras, J. L. *Atmos. Environ.* **2006**, *40*, 2575–2582.
34. Lewis, C. W.; Klouda, G. A.; Ellenson, W. D. *Atmos. Environ.* **2004**, *38*, 6053–6061.
35. Lewis, C. W.; Stiles, D. C. *Aerosol. Sci. Technol.* **2006**, *40*, 189–196.
36. Bench, G.; Fallon, S.; Schichtel, B.; Malm, W.; McDade, C. *J. Geophys. Res.* 2007, *112*, D10205, doi:10.1029/2006JD007708.
37. Gaffney, J. S.; Marley, N. A.; Tackett, M.; Gunawan, G.; Sturchio, N. C.; Heraty, L.; Martinez, N.; Hardy, K. *Proceedings of the AMS National Meeting, New Orleans*; 2008, Paper J1.1.
38. Aiken, A. C.; de Foy, B.; Wiedinmyer, C.; DeCarlo, P. F.; Ulbrich, I. M.; Wehrli, M. N.; Szidat, S.; Prevot, A. S. H.; Noda, J.; Wacker, L.; Volkamer, R.; Fortner, E.; Wang, J.; Laskin, A.; Shutthanandan, V.; Zheng, J.; Zhang, R.; Paredes-Miranda, G.; Arnott, W. P.; Molina, L. T.; Sosa, G.; Querol, X.; Jimenez, J. L. *Atmos. Chem. Phys.* **2010**, *10*, 5315–5341.
39. Allen, D. Progress Report, Environmental Protection Agency Technology Transfer Network Ambient Monitoring Technology Information Center; 2001, http://www.epa.gov/ttnamti1/houprog.html.
40. Lemire, K. R.; Allen, D. T.; Klouda, G. A.; Lewis, C. W. *J. Geophys. Res.* **2002**, *107*, 4613–4620.
41. Tanner, R. L.; Parkhurst, W. J.; McNicol, A. P. *Aerosol. Sci. Technol.* **2004**, *38*, 133–139.
42. Szidat, S.; Jenk, T. M.; Gäggeler, H. W.; Synal, H. -A.; Fisseha, R.; Baltensperger, U.; Kalberer, M.; Samburova, V.; Wacker, L.; Saurer, M.; Schwikowski, M.; Hajdas, I. *Radiocarbon* **2004**, *46*, 475–484.
43. Bench, G. *Environ. Sci. Technol.* **2004**, *38*, 2424–2427.
44. Yamamoto, N.; Muramoto, A.; Yoshinaga, j.; Shibata, K.; Endo, M.; Endo, O.; Hirabayashi, M.; Tenabe, K.; Goto, S.; Yoneda, M.; Shibata, Y. *Environ. Sci. Technol.* **2007**, *41*, 6357–6362.
45. May, B.; Wagenbach, D.; Hammer, S.; Steier, P.; Puxbaum, H.; Pio, C. *Tellus* **2009**, *61*, 461–472.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

46. Takahashi, K.; Hirabayashi, M.; Tanabe, K.; Shibata, Y.; Nishikawa, M.; Sakamoto, K. *Water, Air, Soil Pollut.* **2007**, *185*, 305–310.
47. Tanner, R. L.; Gaffney, J. S.; Phillips, M. F. *Anal. Chem.* **1982**, *54*, 1627–1630.
48. Handa, D.; Nakajima, H.; Arakaki, T.; Kumata, H.; Shibata, Y.; Uchida, M. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2010**, *268*, 1125–1128.
49. Finlayson-Pitts, B. J.; Pitts, J. N. In *Chemistry of the Upper and Lower Atmosphere*; Academic Press: San Francisco, CA, 2000.
50. Lamb, B.; Guenther, A.; Gay, D.; Westberg, H. *Atmos. Environ.* **1987**, *21*, 1695–1705.
51. Lubowski, R. N.; Versterby, M.; Bucholtz, S.; Baez, A.; Roberts, M. J. *USDA publication ElB14.* 2002; http://www.ers.usda.gov/publications/EIB14/eib14a.pdf.
52. McCarty, J. L.; Justice, C. O.; Korontzi, S. *Remote Sens. Environ.* **2007**, *108*, 151–162.
53. Sage, R. F. *Plant Biol.* **2001**, *3*, 202–213.
54. Yokelson, R. J.; Urbanski, S. P.; Atlas, E. L.; Toohey, D. W.; Alvarado, E. C.; Crounse, J. D.; Wennberg, P. O.; Fisher, M. E.; Wold, C. E.; Campos, T. L.; Adachi, K.; Buseck, P. R.; Hao, W. M. *Atmos. Chem. Phys.* **2007**, *7*, 5569–5584.
55. Yokelson, R.; Crounse, J. D.; DeCarlo, P. F.; Karl, T.; Urbanski, S.; Atlas, E.; Campos, T.; Shinozuka, Y.; Kapustin, V.; Clarke, A. D.; Weinheimer, A.; Knapp, D. J.; Montzka, D. D.; Holloway, J.; Weibring, P.; Flocke, F.; Zheng, W.; Toohey, D.; Wennberg, P. O.; Wiedinmyer, C.; Mauldin, L.; Fried, A.; Richter, D.; Walega, J.; Jimenez, J. L.; Adachi, K.; Buseck, P. R.; Hall, S. R.; Shetter, R. *Atmos. Chem. Phys.* **2009**, *9*, 5785–5812.
56. Fischer, E. V.; Jaffe, D. A.; Marley, N. A.; Gaffney, J. S.; Marchany-Rivera, A. *J. Geophys. Res.* **2010**, *115*, D20209, doi:10.1029/2010JD013943.
57. ORNL, Oak Ridge National Laboratories. *Bioenergy Information Feedstock Network*; 2010, http://bioenergy.ornl.gov/.
58. Marley, N. A.; Gaffney, J. S.; Kelley, K. L.; Sarkar, A.; Bridges, G. L. *Eos Trans. AGU, Fall Meet. Suppl.* **2009**, *90*, A13C–0241.
59. Garber, E. R.; Rudich, Y. *Atmos. Chem. Phys.* **2006**, *6*, 729–753.
60. Avery, G. B; Willey, J. D.; Kieber, R. J. *Atmos. Environ.* **2006**, *40*, 7539–7544.
61. Subramanian, R.; Kok, G. L.; Baumgardner, D.; Clarke, A.; Shinozuka, Y.; Campos, T. L.; Heizer, C. G.; Stephens, B. B.; de Foy, B.; Voss, P. B.; Zaveri, R. A. *Atmos. Chem. Phys.* **2010**, *10*, 219–237.

Downloaded by PENNSYLVANIA STATE UNIV on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch015

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Chapter 16

Mitigating Greenhouse Gas Emissions from Agroecosystems: Scientific Basis and Modeling Approach

Changsheng Li[*]

Institute for the Study of Earth, Oceans, and Space,
University of New Hampshire, Durham, NH 03824, U.S.A.
[*]E-mail: Changsheng.li@unh.edu

The greenhouse gases (GHGs) commonly observed in agroecosystems, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), are byproducts of survival of the microorganisms living in soil, manure or animal enteric systems. When environmental redox potential (i.e., Eh) evolves between 650 and -350 mV, different groups of the microbes can be activated to gain energy by transferring electrons between corresponding reductive and oxidative agents. When oxygen, nitrate or carbon is utilized as electron acceptor under the varied Eh conditions, CO_2, N_2O or CH_4 will be produced, respectively. It is the spatial and temporary coincidence of the three controlling factors (i.e., Eh, electron donor and electron acceptor) that results in production of the three gases. If any of the factors is limited or missing, the greenhouse gas production will be reduced or eliminated. This is the principle that guides us to mitigate greenhouse gas emissions from agroecosystems by altering management practices. To quantify impacts of management alternatives on the microbe-mediated redox reactions, process-based models have been developed to integrate the reactions with a group of environmental driving forces. A biogeochemical model, Denitrification-Decomposition or DNDC, was adopted in the study to explain how this kind of models can be constructed and how they could serve the GHG mitigation. Three case studies for mitigating agricultural CO_2, N_2O and CH_4 emissions

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

are described in the paper to demonstrate how to assess effectiveness of management alternatives with the modeling approach.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Fluxes of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), three major greenhouse gases (GHGs), are detected across almost all agro-ecosystems worldwide. During the period of earth evolution, the three gases played an important role in shaping the planetary climate and reforming the ecosystems. However, faced by the threats of contemporary climate change, people are longing to moderate the increasing trends of the gases in the atmosphere. Agro-ecosystems are apparently an ideal target for doing so due to their accessibility and manageability. How are the GHGs produced in agroecosystems? What farming management alternatives could mitigate the GHG emissions? How can we quantify effectiveness of the candidate mitigation options? This paper is going to answer the questions based on the latest developments in research.

Greenhouse Gases, Byproducts of Microbial Survival

Carbon dioxide, CH_4 or N_2O can be produced in any environment where organic matter and microbes co-exist. In most agroecosystems, organic matter and microorganisms are the major players dominating soil fertility and nutrient cycles including carbon (C) and nitrogen (N) gas productions. In chemistry, the production of CO_2, N_2O or CH_4 results from typical reductive-oxidative (or redox) reactions, which are characterized with electron exchange between reductants and oxidants. So the occurrence of the redox reactions is theomodically controlled by the environmental redox potential (Eh); and the reaction rates are determined by the concentrations of the coupled electron donors and acceptors. The microbes living in the systems play a key role in the process, who gain energy by transferring the electrons that results in GHG production (*1*)

CO_2

Under aerobic conditions, the microbes living in soil or manure gain energy by breaking down the C bonds of the organic compounds existing in the same ecosystem. During the process, electrons are released from the C and must transfer to an electron acceptor. The electron acceptors or oxidants commonly existing in the soil or manure include oxygen (O_2), nitrate (NO_3^-), 4-valent manganese (Mn^{4+}), ferric ion (Fe^{3+}) and sulfate (SO_4^{2-}). Among the oxidants, O_2 possesses the lowest Gibbs free energy and, hence, is the first candidate electron receiver. During the electron transfer occurring in the microbial cells, the ionized oxygen combines with the dissociated C to form CO_2 while releasing the CO_2 formation energy ($\Delta_f G^\circ = -94.26$ kcal/mol). In biology, the process is called as microbial heterotrophic respiration. For any soil or manure system if it is well aerated, emissions of CO_2

from the system are always expectable. It is the major process that leads to the losses of organic C from agroecosystems into the atmosphere.

N_2O

Soil redox potential (Eh) varies driven by a number of natural or management factors. For example, during a rainfall or irrigation event, the top soil could be saturated by water, and hence diffusion of the atmospheric O_2 into the soil profile will be blocked. Along with depletion of the residue O_2 left in the soil pores, most of the soil decomposers relying on O_2 as electron acceptor will be depressed. However, the low Eh conditions will stimulate another group of microbes, which are capable of utilizing nitrate as electron acceptor. Among the soil oxidants, nitrate possesses the second lowest Gibbs free energy, and hence is ready to be used as an electron acceptor when O_2 is depleting in the soil or manure. After receiving an electron, nitrate will become nitrite (NO_2^-). Nitrite can be further reduced to nitric oxide (NO), nitrous oxide (N_2O) and finally dinitrogen (N_2). The sequential reactions are called as denitrification as they lead to the losses of soil N into the atmosphere. During the denitrification processes, N_2O is produced as an intermediate, which can be further involved in the N_2O reduction to be consumed. For example, if a soil or manure system is too wet, the N_2O produced by the nitrate-denitrifiers could be further reduced to N_2 that will result in little N_2O emitted. So the net emission of N_2O is highly sensitive to the soil Eh dynamics. This character should be utilized to mitigate N_2O emissions. Nitrification is another source of soil N_2O but usually with relatively low emissions from most agroecosystems.

CH_4

If an organic matter-microbe co-existing system is under anaerobic conditions for a relatively long-term (e.g., several days or months), the major soil oxidants, such as O_2, nitrate, manganese (Mn^{4+}), iron (Fe^{3+}) and sulfate, will be depleted by the decomposers, denitrifiers, manganese bacteria, iron bacteria and sulfur bacteria, respectively. In the case, the low Eh ($<$-200 mV) status will be built up that stimulates another group of microbes, which survive under the deeply anaerobic conditions. These anaerobic microbes gain energy by breaking down the organic polymers (e.g., carbohydrates, proteins, fats) into their smaller constituent parts such as sugars, amino acids or fatty acids. This process is called hydrolysis. The sugars and amino acids can then be utilized by the acidogenic bacteria to produce CO_2, H_2 and organic acids. Finally, methanogens convert these products to CH_4 by transferring electrons from H_2 to C. As the methanogenesis processes rely on the low Eh and C sources, altering any of the two factors could effectively mitigate CH_4 production in the ecosystems.

In summary, CO_2, N_2O and CH_4 emitted from agroecosystems are nothing but the byproducts of microbial survival during different stages of Eh evolution in the soil or manure systems (Figure 1). In thermodynamics, the occurrences of the processes depend on the environmental Eh. In reaction kinetics, the rates of the processes are determined by concentrations of the relevant electron donors and

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

acceptors. Theoretically, altering any of the three drivers (i.e., Eh, electron donor and electron acceptor) will be able to change the GHG emissions.

Management Options for Mitigating GHG Emissions

In order to mitigating CO_2, N_2O or CH_4 production which is directly controlled by Eh, electron donor and electron acceptor, management options could be assessed in consideration of their impacts on one or more of the three driving factors. Based on the hypothesis, theoretical analyses were conducted to identify the management alternatives that could potentially affect the Eh, electron donor or electron in agroecosystems.

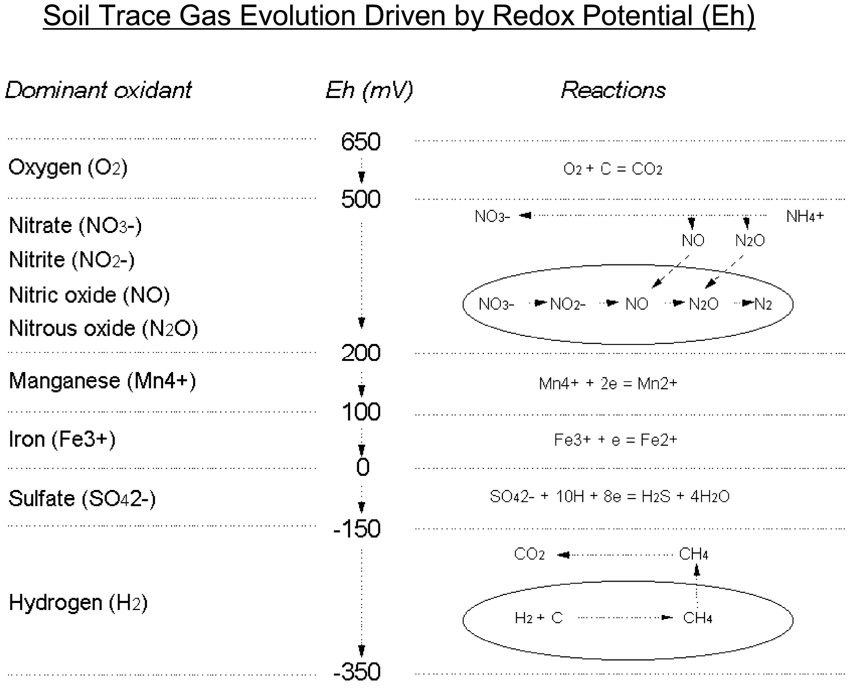

Soil Trace Gas Evolution Driven by Redox Potential (Eh)
Dominant oxidant
Eh (mV)
Reactions
650
Oxygen (O2)
O2 + C = CO2
500
Nitrate (NO3-)
Nitrite (NO2-)
Nitric oxide (NO)
Nitrous oxide (N2O)
NO3-
NH4+
NO
N2O
NO3-
NO2-
NO
N2O
N2
200
Manganese (Mn4+)
Mn4+ + 2e = Mn2+
100
Iron (Fe3+)
Fe3+ + e = Fe2+
0
Sulfate (SO42-)
SO42- + 10H + 8e = H2S + 4H2O
-150
Hydrogen (H2)
CO2
CH4
H2 + C
CH4
-350

Figure 1. CO_2, N_2O, and CH_4 are products of microbe-mediated redox reactions occurring in different stages of the environmental Eh evolution.

Management Practices for Reducing N_2O Emissions

Nitrous oxide is the most important greenhouse gas emitted from agricultural lands in the U.S. However, quantifying N_2O emissions with field measurements has long been remained as a challenge. N_2O emissions are highly variable in space and time. It has been widely observed that a few episodes of N_2O fluxes could contribute a big portion of the annual emissions. Decades-long researches indicate that the emission episodes result from the spatial and temporary coincidence of three major drivers, i.e., Eh, dissolved organic carbon (DOC) and available N. For example, in some soils or manure storages which are rich in both DOC and nitrate, a sudden decrease in the environmental Eh would trigger denitrification to induce a surge flux of N_2O. A number of natural or management events have been identified to be able to trigger the episodic N_2O emissions by altering the environmental Eh or DOC or nitrate concentration. The events include rainfall, irrigation, fertilizer application, manure or litter amendment, and soil freezing/thawing. In the microbe-mediated process, DOC and nitrate serve as electron donor and acceptor, respectively, and hence determine the reaction rates. Table 1 suggests a group of management practices, which could alter the status of Eh, DOC or available N in soil or manure systems to eliminate the synchronous co-existance of the three factors.

Some of the listed options in Table 1 have been applied in the U.S. or other countries with promising results. Optimizing fertilizer application rates, using control-release fertilizers or nitrification inhibitor have been studies with positive results in N_2O reduction. However, a thorough examination for the options has not been done with either field experiments or modeling simulations.

Management Practices for Reducing CH_4 Emissions

Methane is emitted from flooded rice fields or other wetland ecosystems. Methanogens utilize H_2 and C to produce CH_4 to gain energy ($\Delta_f G° = -31$ kcal/mole). The process occurs with optimum growth Eh as <-200mV, optimum temperature 55°C and optimum pH 2. If any oxidants such as O_2, nitrate, Mn^{4+}, Fe^{3+} or sulfate are introduced in the deep anaerobic conditions, the H_2 will be consumed and the CH_4 production will cease. In theory, there are two ways to reduce CH_4 emissions from wetland agroecosystems: elevating the soil Eh status or decreasing C availability. Table 2 provides management options which could potentially reduce CH_4 emissions from wetland agroecosystems.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Table 1. Agricultural management options for mitigating N_2O emissions from agroecosystems

Target factor to change	*Mitigation option*	*Feasibility*
Redox potential (Eh)	Action: Loosen compacted soils in grazed pastures. Effect: Elevate soil Eh during rainfall or irrigation events. Result: Reduce denitrification-induced N_2O , but affect C sequestration.	*
	Action: Change soil texture by adding sand, silt or clay. Effect: Alter soil aeration status. Result: Reduce denitrification-induced N_2O, but could affect C sequestration.	*
	Action: Convert cultivated organic soils into wetland conditions. Effect: Build up deeply anaerobic conditions. Result: Eliminate both nitrification- and denitrification-induced N_2O, but could increase CH_4 emissions.	*
	Action: Reduce frequency of flooding and drainage cycles in wetland soils. Effect: Reduce soil decomposition and nitrification but enhance denitrification. Result: Eliminate both nitrification- and denitrification-induced N_2O, but could increase CH_4 emission	*
Dissolved organic carbon (DOC)	Action: Reduce organic matter (litter or manure) incorporation in soils. Effect: Decrease DOC with low decomposition rates. Result: Reduce both nitrification- and denitrification-induced N_2O, but affect C sequestration.	*
	Action: Decrease quality of organic matter inputs. Effect: Decrease DOC by reducing decomposition rates. Result: Reduce both nitrification- and denitrification-induced N_2O, and maintain C sequestration.	**
	Action: Convert the upland with organic soils into wetland Effect: Decrease DOC by depressing decomposition. Result: Reduce both nitrification- and denitrification-induced N_2O, may reduce CO_2 emissions from loss of soil organic carbon, but may increase CH_4 emissions.	*

Continued on next page.

Table 1. (Continued). Agricultural management options for mitigating N_2O emissions from agroecosystems

Target factor to change	*Mitigation option*	*Fea-si-bil-ity*
Available nitrogen	Action: Optimize N fertilizer application rates based on soil fertility and crop demand. Effect: Reduce N availability to nitrifiers and denitrifiers. Result: Reduce nitrification- and denitrification-induced N_2O, increase fertilizer use efficiency, maintain optimum yield	***
	Action: Apply nitrification or urease inhibitors. Effect: Reduce nitrate availability to denitrifiers. Result: Reduce nitrification- and denitrification-induced N_2O.	**
	Action: Precisely schedule the timing of fertilizer applications. Effect: Increase fertilizer use efficiency, reduce N availability for nitrifiers and denitrifiers. Result: Reduce nitrification- and denitrification-induced N_2O.	**
	Action: Rotate crops or plant cover crops to reduce excess N in soils. Effect: Increase fertilizer use efficiency, reduce N availability for nitrifiers and denitrifiers. Result: Reduce nitrification- and denitrification-induced N_2O.	**
	Action: Use control-release fertilizers. Effect: Increase fertilizer use efficiency, reduce N availability for nitrifiers and denitrifiers. Result: Reduce nitrification- and denitrification-induced N_2O.	**
	Action: Use fertigation to combine irrigation with fertilization. Effect: Increase fertilizer use efficiency, reduce residue N for nitrifiers and denitrifiers. Result: Reduce nitrification- and denitrification-induced N_2O.	**
	Action: Convert upland with organic soils to wetland. Effect: Depress nitrification and intensify denitrification. Result: Reduce both nitrification- and denitrification-induced N_2O, but increase CH_4 emissions.	*
	Action: Convert intensive to reduced tillage. Effect: Reduce N availability by decreasing mineralization rates. Result: Reduce near-term nitrification- and denitrification-induced N_2O, but may increase long-term N_2O emissions due to elevated soil organic carbon.	*
	Action: Compost organic materials before applying to soil. Effect: Reduce mineralization and consume free N in soil. Result: Reduce both nitrification- and denitrification-induced N_2O. Note: Use anaerobic digesters to pretreat manure or crop residue to eliminate labile N.	**

[*] Note: Substantial negative environmental effects in most locations; often too expensive. [**] Negative environmental effects in some situations; often too expensive. [***] Typically no negative environmental effects; financially feasible.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Table 2. Agricultural management options for mitigating CH_4 emissions from agroecosystems

Target factor	*Mitigation option*	*Feasibility*
Redox potential (Eh)	Action: Decrease number and duration of floodings of rice field soils. Effect: Periodically elevate soil redox potential. Result: Reduce CH_4 emission, save water, increase crop yields, but increase N_2O emissions.	***
	Action: Apply oxidants (e.g., nitrate, Mn4+, Fe3+, sulfate) for wetland soils. Effect: Elevate soil redox potential temporally. Result: Reduce CH_4 emissions.	*
	Action: Increase soil aeration by converting wetland to upland. Effect: Elevate soil redox potential permanently. Result: Reduce CH_4 emissions, increase N_2O emissions, often reduce C sequestration.	*
	Action: Loosen compacted soils in grazed pastures. Effect: Elevate soil aeration during rainfall events. Result: Reduce CH_4 emissions, increase CO_2 emissions.	*
Dissolved organic carbon (DOC)	Action: Reduce organic matter (crop residue or manure) incorporation in wetland soils. Effect: Decrease DOC with low decomposition rates. Result: Reduce CH_4 emissions, decrease C sequestration.	*
	Action: Incorporate organic matter in low quality in wetland soils. Effect: Decrease DOC by reducing decomposition rates. Result: Reduce CH_4, increase C sequestration, but may reduce soil fertility.	*
	Action: Develop new rice cultivars with low root mass or exudation rates. Effect: Decrease root-produced DOC. Result: Reduce CH_4 production.	*
	Action: Reduce plant biomass in natural wetlands Effect: Decrease root-induced DOC, reduce CH_4 aerenchyma transport. Result: Reduce CH_4 emissions, but decrease C sequestration.	*
	Action: Apply crop straw or manure in rice paddies before transplanting or after harvest. Effect: Decrease availability of straw-decomposition-induced DOC to methanogens. Result: Reduce CH_4 emissions.	**

Continued on next page.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Table 2. (Continued). Agricultural management options for mitigating CH_4 emissions from agroecosystems

Target factor	*Mitigation option*	*Feasibility*
Gas transport	Action: Replace rice breeds with cultivars that have barriers to gas transport in stems and roots. Effect: Eliminate pathway for gas transport. Result: Reduce CH_4 emissions.	*
	Action: Replace rice vascular plants with nonvascular plants in natural wetlands. Effect: Eliminate pathway for gas transport. Result: Reduce CH_4 emissions.	*

* Note: Substantial negative environmental effects in most locations; often too expensive. ** Negative environmental effects in some situations; often too expensive. *** Typically no negative environmental effects; financially feasible.

Midseason-drainage has been widely adopted in many rice-producing countries in Asia (e.g., China, India, Japan, Thailand etc.) resulting in significant reductions in CH_4 emissions from the rice fields (*2*). Other options remain to be tested with more field experiments.

Management Practices for Reducing CO_2 Emissions

There are quite a number of C exchange fluxes occurring at the interface between the atmosphere and agroecosystems, which include photosynthesis, plant autotrophic respiration, plant litter incorporation, root exudation, soil microbial heterotrophic respiration etc. However, some of the C fluxes such as photosynthesis and plant autotrophic respiration don't directly count for net C exchange between the atmospheric and terrestrial ecosystems. Only the C that can be "permanently" sequestered in the terrestrial soils or sediments is regarded as a net contribution. For agroecosystems, the dynamics of soil organic carbon (SOC) content is determined by the balance between the SOC gain through plant litter incorporation and the SOC loss induced by the microbial heterotrophic respiration. Increasing the litter incorporation rate or decreasing the microbial respiration rate will inherently favor SOC accumulation in the agroecosystems. The relationship among net C sequestration, litter incorporation, microbial respiration and environmental drivers is shown in Figure 2. Since both crop biomass production or soil microbial respiration are controlled by a same group of driving factors such as climate, soil texture and farming management practices, any change in the factors will alter the soil C sequestration rates by simultaneously affecting the litter production and microbial respiration. For an ecosystem, if the environmental factors could keep constant for a long-term (e.g., >150 years), the

SOC storage would eventually approach to equilibrium. The SOC content at the equilibrium can be regarded as the C sequestration capacity of the soil (Figure 3). The difference between the capacity and the current SOC content is the potential of C sequestration for the soil. In reality, any of the driving factors cannot keep constant in decades or centuries, and hence the prospective SOC equilibrium value for most agroecosystems will be ever contantly readjusted. The actual SOC sequestration rate can be calculated only based on the moving target. The most popular management options for increasing litter incorporation or decreasing soil decomposer activity by reducing the soil or manure Eh are listed in Table 3.

Driven by the current C sequestration campaigns, some of the listed alternative practices in Table 3 have been tested with promising results. No-till has been adopted by the majority U.S. farmers to prevent their soils from erosion meanwhile elevated the surface SOC contents. In China, a nation-wide campaign has been launched to encourage the farmers to incorporate more crop residues into the soils that has significantly elevated the C sequestration rates in the agroecosystems across the country during the past two decades.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

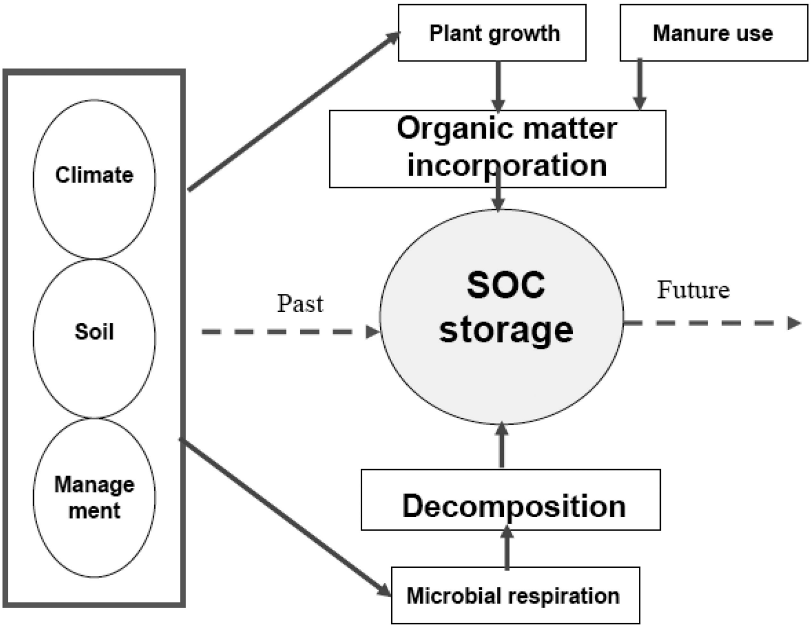


Figure 2. Dynamics of soil organic carbon (SOC) storage is determined by the balance between the SOC gain from organic matter incorporation and the SOC loss induced by microbial heterotrophic respiration.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

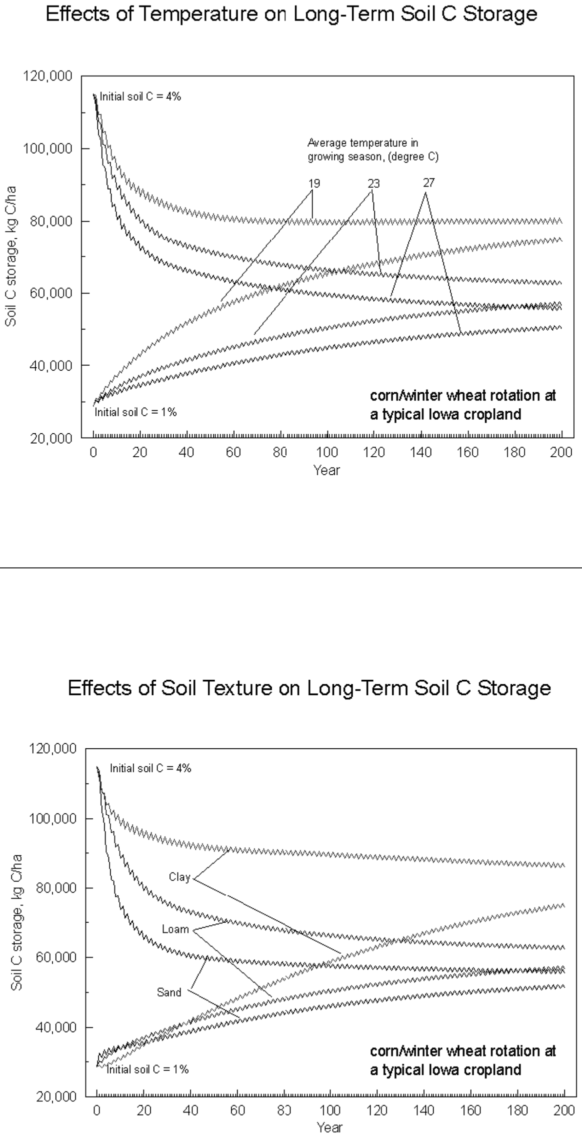


Figure 3. Soil organic carbon (SOC) content will approach to equilibrium whose level is determined by the environmental drivers including climate, soil texture and farming management practices.

Table 3. Agricultural management options for mitigating net CO_2 emissions from agroecosystems

Target factor	*Mitigation option*	*Feasibility*
Soil C input	Action: Increase incorporated fraction of crop residue after harvest. Effect: Increase annual SOC input rate by elevating prospective C sequestration capacity. Result: Increase soil C sequestration, but could increase N_2O emissions.	**
	Action: Utilize organic fertilizers (e.g., manure, compost etc.). Effect: Increase annual SOC input rate by elevating prospective C sequestration capacity. Result: Increase soil C sequestration, but could increase N_2O emissions.	***
	Action: Incorporate inorganic C (e.g., biochar) or composted/digested litter in soil. Effect: Increase soil C input, decrease labile SOC content. Result: Increase soil C sequestration, could affect N_2O emissions due to increased cation exchange capacity.	**
	Action: Plant cover crops or high biomass crops to increase litter incorporation. Effect: Increase SOC input rate. Result: Increase soil C sequestration, and could decrease N_2O emissions.	***
Soil redox potential (Eh)	Action: Convert conventional tillage to reduced tillage or no-till. Effect: Depressing soil decomposers' heterotrophic respiration by decreasing oxygen concentration in soil profile due to reduced physical disturbance. Result: Reduce CO_2 emissions, but may increase N_2O emissions.	***
	Action: Decrease soil aeration by converting upland to wetland. Effect: Depressing soil decomposers' heterotrophic respiration in saturated soil. . Result: Reduce CO_2 emissions, but increase CH_4 emissions.	**
	Action: Convert cropland to forest or pasture. Effect: Increase biomass/litter production/incorporation, decrease soil disturbance. Result: Reduce CO_2 emissions.	
	Action: Incorporate litter into deep layers of soil profile using special tilling method. Effect: Decrease redox potential and microbial population	*

Continued on next page.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Table 3. (Continued). Agricultural management options for mitigating net CO_2 emissions from agroecosystems

Target factor	*Mitigation option*	*Feasibility*
	around fresh litter. Result: Reduce CO_2 emissions.	

* Note: Substantial negative environmental effects in most locations; often too expensive. ** Negative environmental effects in some situations; often too expensive. *** Typically no negative environmental effects; financially feasible.

In summary, there are quite a number of management options that possess potential to mitigate CO_2, N_2O or CH_4 emissions from agroecosystem. However, the effectiveness of the alternative practices highly depends on the ecological drivers including climate, soil properties, vegetation and other farming management practices. Any single change in the primary drivers would simultaneously affect several of environmental factors such as soil temperature, moisture, pH, Eh and substrate concentration gradients; and these environmental factors will turn to simultaneously and collectively affect a series of biochemical or geochemical reactions, which determine the GHG production and consumption in the ecosystems (Figure 4). It is essential for quantifying the GHG impacts of management alternatives to bring them into context of the intricate interactions among the primary drivers, the environmental factors and the biogeochemical reactions. Process-based models were developed to handle the complex systems. This paper uses one of the models as an example to illustrate how this kind of models could help with assessment of mitigation options.

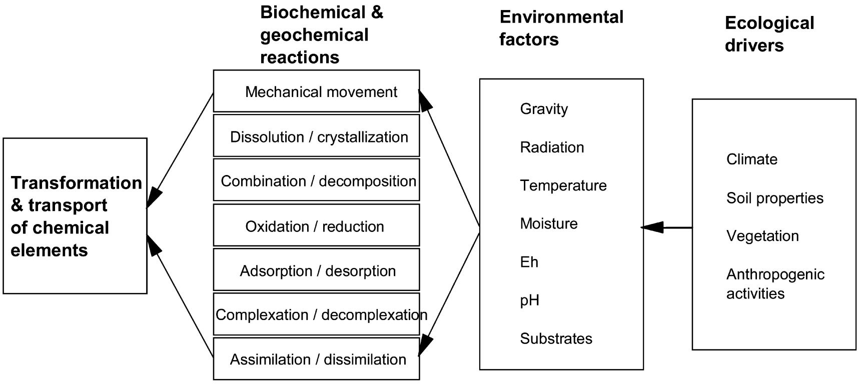

Biochemical & geochemical reactions
Environmental factors
Ecological drivers
Mechanical movement
Dissolution / crystallization
Combination / decomposition
Oxidation / reduction
Adsorption / desorption
Complexation / decomplexation
Assimilation / dissimilation
Transformation & transport of chemical elements
Gravity
Radiation
Temperature
Moisture
Eh
pH
Substrates
Climate
Soil properties
Vegetation
Anthropogenic activities

Figure 4. Biogeochemical cycles of chemical elements are driven by a series of biochemical and geochemical reactions, whose occurrences and rates are determined by a biogeochemical field consisting of a number of environmental factors. The environmental factors vary in space and time controlled by the ecological drivers.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Assessing Management Alternatives with Modeling Approach

Field experiments provide first-hand information for understanding how farming management practices quantitatively affect GHG emissions. However, most of the agricultural experiments are labor-intense, time-demanding and costly that has hindered them from being a routine approach to test management alternatives at large scale. Process-based models were developed to maximize utilization of the valuable field datasets by integrating them with the basic knowledge accumulated in sciences. With classical laws of physics, chemistry and biology embedded in the modeling framework, the biogeochemical models obtained capacity for interpreting and integrating the datasets observed at specific sites, and extrapolating the understandings gained at sites into regions.

In the early 1990s, a process-based model, Denitrification-Decomposition or DNDC, was developed for quantifying N_2O emissions from the U.S. agricultural soils (*3*, *4*). The model was built upon the basic concepts of biogeochemistry, which define the interactions between life and its inorganic environment by tracking movement of the chemical elements in ecosystems (*5*, *6*). Among the four biogeochemical concepts (i.e., abundance, coupling, cycling and field), the biogeochemical field was adopted as a philosophic basis to integrate all the environmental factors based on their direct or indirect effects on GHG production and consumption in soils. A biogeochemical field is the assemblage of forces which control the elementary movement in ecosystems. For most agro-ecosystems, the forces or factors controlling the elementary movement include gravity, radiation, temperature, moisture, Eh, pH and substrate concentration gradient. These factors construct a multi-dimensional field, which controls the elementary transport and transformation. Those environmental factors ever vary in space and time driven by a few of primary drivers such as climate, soil, vegetation and anthropogenic activity. A biogeochemical model can be constructed by building up two bridges to link the primary drivers to the environmental factors, and then to link the environmental factors to the biochemical or geochemical reactions that shape the biogeochemical cycling of the chemical elements. The most common biogeochemical processes controlling elemental movement include mechanical movement, dissolution/crystallization, decomposition/combination, oxidation/reduction, adsorption/desorption, complexation/decomplexation, and assimilation/dissimilation (Figure 4). These processes determine the elemental movement in space and time governed by the laws of thermodynamics and reaction kinetics. Through the elemental cycling, life interacts with and shapes its environment by means of exchanges of energy, matter and information. The DNDC model was established based on the biogeochemical concepts but with a focus on only two chemical elements, C and N in its current status.

In DNDC, any single change in the primary drivers (e.g., climate, soil, vegetation or anthropogenic activity) can simultaneously alter one or more of the environmental factors (e.g., radiation, temperature, moisture, Eh, pH and substrate concentration gradient); and the changes in the environmental factors can collectively affect several biochemical or geochemical reactions, which finally determine the transport and transformation of C and N in the ecosystem. For

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

example, a change in irrigation could simultaneously alter the soil temperature, moisture, Eh, and concentrations of DOC, ammonium or nitrate; these changes will simultaneously and collectively affect the rates of decomposition, nitrification and denitrification occurring in the soil, that will eventually alter the production, consumption and emission of N_2O in the soil. The correlation between the cause (i.e., a change in irrigation for this example) and the consequence (N_2O fluxes) is inherently nonlinear. In addition, the extreme spatial and temporal heterogeneity of many of the primary drivers has obscured the relationship between the causes and effects for many of the biogeochemical processes. DNDC was developed to handle the complexity.

The core of DNDC was built upon two classical equations, the Nernst equation and the Michaelis-Menten equation. The Nernst equation is a thermodynamic formula defining the environmental Eh status based on concentrations of the dominant oxidants and reductants co-existing in the domain system (*7*):

$$Eh = Eo + RT/nF * \ln([O]/[W]) \quad [1]$$

where Eh is redox potential (volts), Eo is standard redox potential (volts), R is gas constant, T is temperature in Kelvin, n is number of the electrons transferring in the redox reaction, F is Faraday constant, [O] is concentration of oxidant (mol/L), and [W] is concentration of reductant (mol/L).

The Michaelis-Menten equation is a widely applied formula to describe the kinetics of microbial growth with dual nutrients in biology (*8*):

$$R = Rmax * DOC/(Ka+DOC) * [O]/(Kb+[O]) \quad [2]$$

where R is reaction rate, Rmax is maximum reaction rate, DOC is concentrations of dissolved organic C, [O] is concentrations of oxidant, and Ka and Kb are half-saturation constants for substrates DOC and oxidant, respectively.

Since the Nernst and Michaelis-Menten equations share a common item, oxidant concentration ([O]), the two equations can be integrated into a computable framework. A kinetic scheme, "anaerobic balloon", was invented in DNDC to integrate the Nernst and Michaelis-Menten equations. The "anaerobic balloon" is defined as the volumetric fraction of anaerobic micro-sites in a domain soil or manure. The size of the balloon varies between 0 and 1 representing the fully aerobic and fully anaerobic conditions, respectively. With the Nernst equation, DNDC calculates soil bulk Eh based on the concentrations of oxygen, nitrate or other dominant oxidants, and then determines the size of the anaerobic balloon based on the modeled Eh value. The balloon divides the domain into two parts: relatively anaerobic microsites within the balloon and relatively aerobic outside the balloon. Based on the size of the balloon, substrates (e.g., DOC, ammonium, nitrate etc.) will be proportionally allocated into the aerobic and anaerobic fractions. It is defined that all the substrates allocated within the balloon will participate in the reductive reactions (e.g., denitrification, CH_4 production etc.); and all the substrates allocated outside the balloon will participate in the oxidative reactions (e.g., nitrification, CH_4 oxidation etc.). Given the substrate contents partitioned into the aerobic and anaerobic fractions, rates of the relevant oxidative and reductive reactions will be calculated based on the Michaelis-Menten

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

equation. Along with the reactions proceeding, the relevant substrates will be consumed that will lead to changes in the bulk Eh of the domain based on the Nernst equation. Thus, computing the loop of "Eh definition—substrate allocation—redox reaction—substrate consumption—Eh redefinition", DNDC tracks the evolution of soil Eh as well as the microbe-mediated redox reactions to produce CO_2, N_2O or CH_4 (Figure 5). In fact, DNDC simulates a series of anaerobic balloons driven by different electron acceptors (O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}). If a soil is fully aerobic (Eh ~650 mV), O_2 will be the dominant electron acceptor used by the soil microbes. In the case, CO_2 is the major gas produced in the soil. During a rainfall or irrigation event, the soil O_2 can be gradually depleted to drive the oxygen-driven anaerobic balloon to swell. Within the anaerobic faction of the soil or manure, when O_2 is depleted the next electron acceptor, nitrate, will be utilized by the soil microbes. Through the sequential denitrification reactions, NO, N_2O and N_2 will be sequentially produced. When the soil nitrate is depleted, the nitrate-driven balloon will burst and another balloon driven by Mn^{4+} will arise. If the soil anaerobic conditions last long enough, all the major electron acceptors (e.g., O_2, nitrate, Mn^{4+}, Fe^{3+} and sulfate) can be depleted that will drive the soil Eh to –150 mV or lower. In the case, methanogens will be stimulated to use H_2 and C to produce CH_4. Thus, by tracking the swelling or shrinking of a series of anaerobic balloons, DNDC is able to simulate the production and consumption of CO_2, N_2O or CH_4 in different stages of the soil Eh evolution (Figure 6). Equipped with the basic thermodynamic and reaction kinetic processes, DNDC is capable of simulating GHG emissions in spite of the difference in climate conditions, soil types or management regimes. During the past two decades, DNDC has been tested against GHG emission datasets observed worldwide with encouraging results *(e.g.,* (*9–26*)*)*. A number of papers have been published during the past two decades to specify the input and output parameters, calibration and validation tests, upscaling and uncertainty of the DNDC model *(see a summary by* (*24*)*)*, which are not redescribed in this paper.

As part of the preimary driving forces, a number of farming management practices have been parameterized in DNDC for assessing their impacts on GHG emissions from a wide range of agroecosystems such as cropland, grassland/pasture, forest, wetland and livestock farm. Table 4 summarizes the management practices included in DNDC.

DNDC predicts impacts of change in management practices on GHG emissions by calculating effects of the management change on the environmental factors (e.g., temperature, moisture, Eh, pH, substrate concentration gradient) first, and then tracking their effects on the microbe-mediated reactions (e.g., decomposition, nitrification, denitrification, fermentation). Best management practices will be identified by comparing the net GHG emissions modeled with the candidate management alternatives. Below-provided are three case studies to demonstrate how DNDC can be utilized to quantify impacts of change in management practices on N_2O, CH_4 or CO_2 emissions for agroecosystems.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

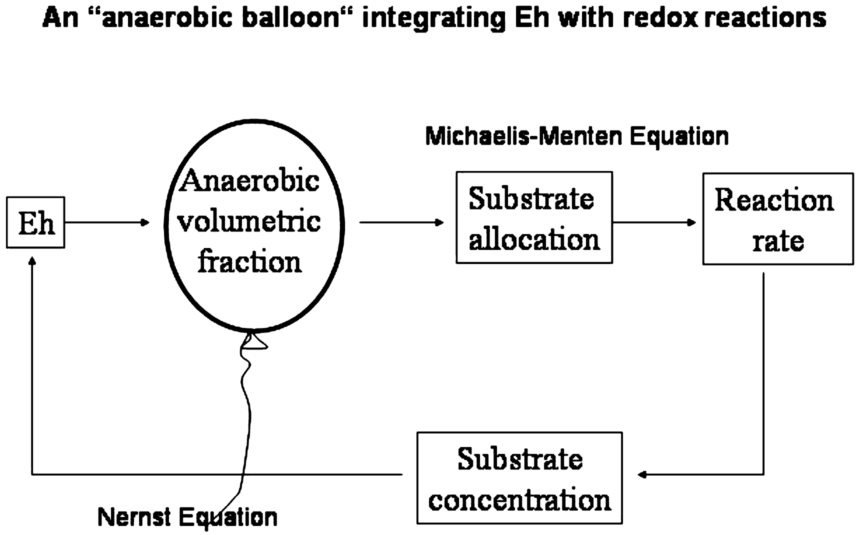

An "anaerobic balloon" integrating Eh with redox reactions
Michaelis-Menten Equation
Eh
Anaerobic volumetric fraction
Substrate allocation
Reaction rate
Substrate concentration
Nernst Equation

Figure 5. An "anaerobic balloon" was invented in the DNDC model to integrate the Nernst equation and the Michaelis-Menten equation to simulate soil Eh dynamics and microbial activities, which lead to production of CO_2, N_2O or CH_4 in different stages of the Eh evolution.

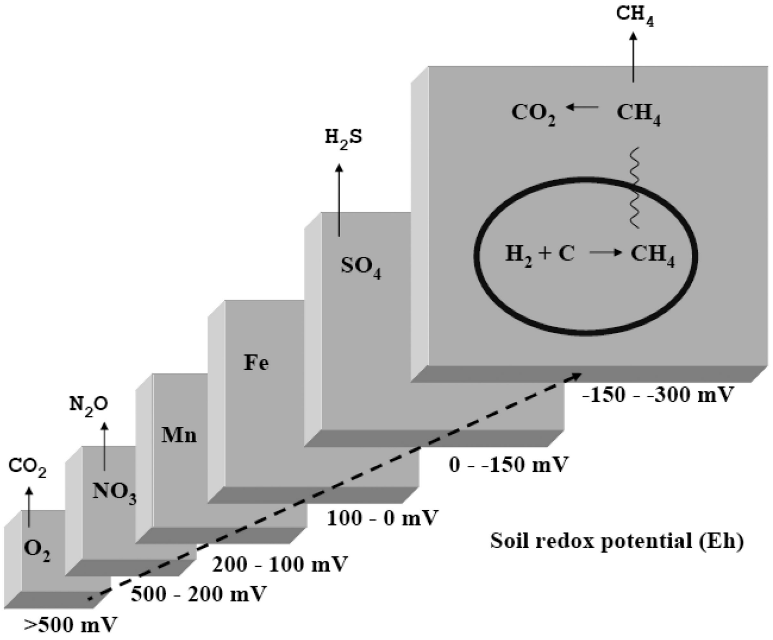

CH_4
CO_2 ← CH_4
$H_2 + C \rightarrow CH_4$
H_2S
SO_4
Fe
Mn
N_2O
NO_3
CO_2
O_2
-150 - -300 mV
0 - -150 mV
100 - 0 mV
200 - 100 mV
500 - 200 mV
>500 mV
Soil redox potential (Eh)

Figure 6. In DNDC, a series of anaerobic balloons driven by O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} and C, respectively, to produce trace gases during the soil Eh evolution.

Table 4. Agricultural management practices parameterized in the DNDC model

Agro-ecosystem	*Practice*	*Specifications*
Cropland or pasture	Crop type	- About 50 major crops are parameterized with their physiological and phenology data based on the USDA and FAO databases;
		- Cover crops are included;
		- Perennial crops are included;
		- Fruit and tea trees are included;
		- A tool program "Crop Creator" is provided for the users to modify the existing crops or create new crops.
	Crop rotation	- Up to six crops can be consecutively or simultaneously planted at a site;
		- Multi-year rotations can be created with complex rotation systems;
		- Upland and wetland cultivations can be rotated;
		- Cropland and grassland can be rotated.
	Tillage	- Conventional tillage with moldboard;
		- Reduced tillage with disk or chisel;
		- No-till;
		- Litter-burying till.
	Fertilization	- Type: urea, ammonium nitrate, ammonium bicarbonate, ammonium sulfate, ammonium phosphate, nitrate;
		- Application date;
		- Application rate in kg N/ha;
		- Application depth;
		- Auto-fertilization is optional;
		- Fertigation is optional;
		- Control-release fertilizer is optional;
		- Nitrification inhibitor is optional;
		- Urease inhibitor is optional.

Continued on next page.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Table 4. (Continued). Agricultural management practices parameterized in the DNDC model

Agro-ecosystem	*Practice*	*Specifications*
	Manure amendment	- Type: farmyard manure, slurry, straw, green manure, compost, bean cake, human waste, poultry waste, sewage sledge, meat/blood meal;
		- Manure quality: C/N ratio;
		- Application date;
		- Application rate: kg N/ha;
		- Application method: surface spreading, incorporation.
	Irrigation	- Based on irrigation events or index;
		- Application rate: mm water per event;
		- Application date;
		- Application method: flood, sprinkler, drip.
	Flooding	- Manual flooding/draining methods: continuous flooding, midseason drainage, marginal flooding;
		- Rainfed: water-table is automatically regulated by precipitation;
		- Water-table is controlled with observed data;
		- Water-table is controlled with empirical equation.
	Plastic cultivation	- Greenhouse: duration and ventilation;
		- Plastic mulching: duration, film color and transparency.
	Cutting/ pruning	- Cutting date;
		- Cut part: fruit, leaf, stem or root;
		- Cut fraction.
	Grazing	- Time periods;
		- Livestock type: cattle, horse, sheep;
		- Intensity: heads/ha;
		- Grazing hours per day.
Forest	Harvesting	- Upper-story harvest;
		- Under-story chopping;
	Burning	- Date;
		- Burned fraction.

Continued on next page.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Table 4. (Continued). Agricultural management practices parameterized in the DNDC model

Agro-ecosystem	*Practice*	*Specifications*
	Fertilization	- Fertilizer type;
		- Application date;
		- Application rate, kg N/ha.
	Reforestation	- Tree type;
		- Date;
		- Density.
	Floor management	- Litter removal: date, fraction.
Wetland	Water table control	- Manual flooding/draining;
		- Water-table is automatically regulated by precipitation and catchment area;
		- Water-table is controlled with observed data;
		- Water-table is controlled with empirical equation.
	Vegetation/ Plants	- Type: physiological and phenology data
		- Productivity;
		- Biomass partition and C/N ratio;
		- Aerenchyma.
Livestock farm	Herd	- Animal type: dairy cow, beef cow, veal, swine, sheep, poultry;
		- Population: heads per farm or housing.
	Feed	- Quantity, kg DM/head/day;
		- Quality, crude protein%.
	Feedlot	- Area, m2
		- Floor type: concrete, slatted floor with under-floor gutter;
		- Bedding: material (straw, sawdust, manure dry, sand), rate (kg DM), quality (C/N ratio), frequency;
		- Ventilation: natural or fens (m3/second);
		- Manure removal: solid/liquid separation, frequency.

Continued on next page.

Table 4. (Continued). Agricultural management practices parameterized in the DNDC model

Agro-ecosystem	*Practice*	*Specifications*
	Compost	- Density;
		- Storage days;
		- Litter addition: quantity and quality;
		- Compost manure removal.
	Lagoon	- Capacity (m3);
		- Surface area (m2);
		- Coverage: no, loose, tight;
		- Receiving rain water;
		- Slurry drainage frequency.
	Anaerobic digester	- Processing temperature: phychrophilic, mesophilic, or thermophilic;
		- Hydraulic retention time (days);
		- Liquid/solid residue removal frequency.
	Field application	- Manure type;
		- Application date;
		- Application rate: kg N/ha and C/N ratio;
		- Application method: surface spreading, incorporation;
		- Crop type and rotation.

Case Study 1: Mitigating N_2O Emissions from a Crop Field in Germany

Flessa and his colleagues measured N_2O fluxes from a crop field at Scheyern in southern Germany in 1992-1993 (*27*). The field was planted with barley (April 11-August 6, 1992), hay (August 17-December 15, 1992) and sunflower (May 11-September 21, 1993) in rotation. In 1992, synthetic fertilizer of 50 kg N/ha was applied on May 3, and farmyard manure was applied twice on August 17 and December 15, containing 67 and 133 kg N/ha, respectively. In 1993, only synthetic fertilizer of 50 kg N/ha was applied on May 11. The field was conventionally tilled with no irrigation. They reported that a high peak of N_2O emission was measured during January 4-11, 1993, whose flux was 0.59 kg N/ha accounting for 42% of the annual total N_2O emissions (1.4 kg N/ha) from the site.

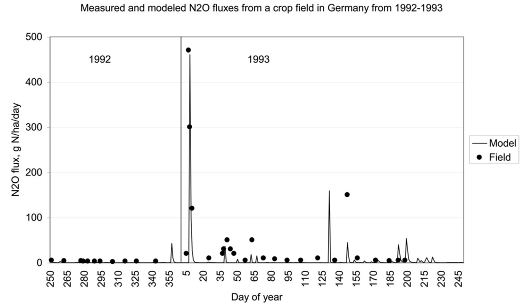
Driven by the input data of local climate, soil properties and cropping management practices, DNDC simulated the soil climate and C and N dynamics in the field. The surge of N_2O emission observed in the January of 1993 was captured by the model (Figure 7a). The modeled data indicated that the application of manure on December 15, 1992 introduced abundant organic matter to the soil

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

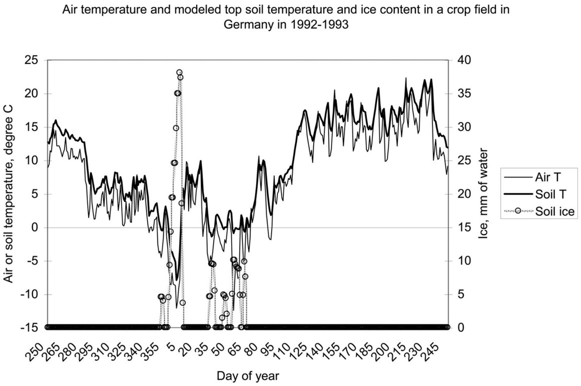
Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

that increased the microbial population as well as nitrate content in the top soil. However, the nitrification process ceased during the period of December 25, 1992-January 6, 1993 (Figure 7c) when the top soil was frozen (Figure 7b). The freeze killed a portion of the microbes and released about 50 kg DOC-C/ha from the microbial cells to the soil. The DOC and nitrate inertly stayed in the frozen soil until January 7, 1993 when the air temperature suddenly increased to about 5°C that melted the soil ice and reactivated the microbes including denitrifiers. Given the abundant DOC and nitrate co-existing in the soil, the thawing water flush stimulated denitrification to produce a surge of N_2O flux.

An alternative management practice was test with DNDC to try reducing the freezing/thawing-induced N_2O fluxes. In the alternative scenario, the date of manure application was moved from December 15, 1992 to March 10, 1993 to avoid the soil freezing/thawing event. The modeled results with the alternative practice showed that the January N_2O surge almost disappeared (Figure 7d). The annual total N_2O flux from the site decreased from 1.4 to 0.62 kg N/ha by simply postponing the manure application date. The crop yields as well as the soil C sequestration rates modeled with the baseline and alternative practices were almost identical. The model application for the German cropland suggested that the freezing/thawing-induced N_2O fluxes could be reduced by altering the manure application date as a low cost mitigation option.



a



b

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

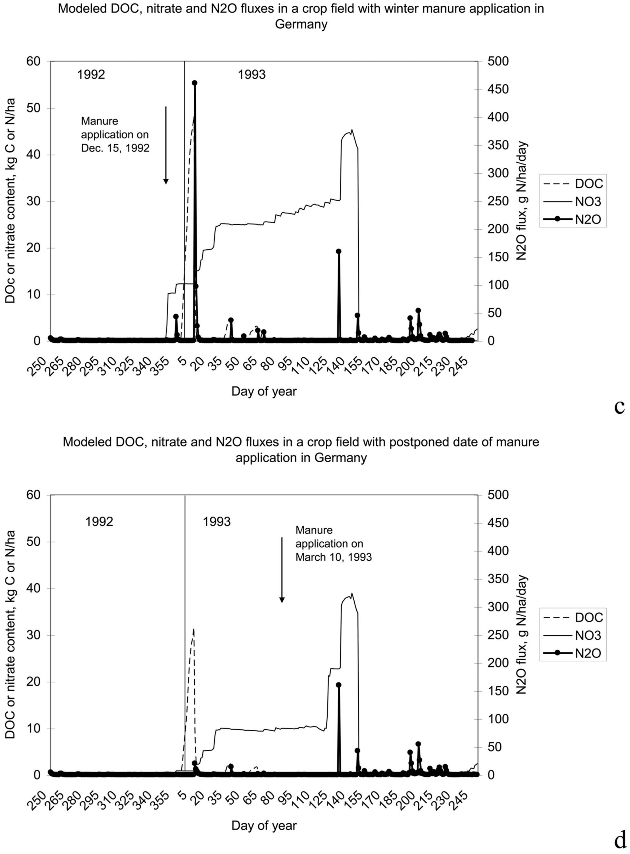


Figure 7. Modeling N_2O emissions from a fertilized crop field in Scheyern, Germany from October of 1992 to September of 1993. (a) Measured and modeled daily N_2O fluxes. (b) Modeled top soil temperature and ice content. (c) Modeled top soil DOC and nitrate contents with the manure application in the winter of 1992. (d) Modeled daily N_2O fluxes and top soil DOC and nitrate contents without manure application in the winter of 1992.

Case Study 2: Mitigating CH_4 Emissions from a Rice Field in California

Under the project "Creating and quantifying carbon credits from voluntary practices on rice farms in the Sacramento Valley" headed by Eric Holst, a dataset of CH_4 fluxes measured at a paddy rice field in Maxwell, California in 1994-1996 were collected for DNDC test. Rice was planted in the field in early May and grew till to early October each year. During the rice growing season, the field was continuously flooded. Urea was applied in rate of 135 kg N/ha at the time of planting. After harvest, all the straw (about 4 tons straw-C) was incorporated in the field and the land was kept flooded during the following winter for water reservation while creating habitants for the migrant birds. Under the baseline management conditions, high CH_4 emissions were observed during the winters of 1994-1996 (Figure 8a).

DNDC was utilized to simulate CH_4 emissions from the field with the baseline management scenario. The modeled results were in agreement with observations (Figure 8a). The modeled data indicated that the coupled farming practices, residue incorporation and land flooding, during the winter seasons stimulated methanogenesis due to the decreased Eh and the elevated DOC concentration in the soil. Two alternative scenarios were designed by decoupling the two faring practices: with straw incorporation but no winter flood (Alternative 1), or with winter flood but no straw incorporation (Alternative 2). The site was re-simulated with DNDC with the same climate and soil conditions but altered flood or straw management scenarios. The modeled results indicated that either of the new practices could substantially decrease CH_4 emissions from the rice field due to the decoupling of the low Eh and high DOC conditions (Figure 8b). Alternative 1 and 2 reduced the CH_4 emissions by 60% and 68%, respectively. Alternative 1 maintained the soil C sequestration rate but increased N_2O emissions due to the lengthened soil aeration period. Alternative 2 substantially reduced the soil C sequestration rate due to no straw amended. Net global warming potential (GWP) was calculated for the baseline and alternative management options based on IPCC's method (i.e., 1 kg CH_4 = 25 kg CO_2-equevalent, and 1 kg N_2O = 320 kg CO_2-equevalent at100-yearhorizon). Based on the net GWP values, Alternative 1 and 2 could reduce the baseline warming contribution by 88% and 59%, respectively (see details in Table 5).

Table 5. DNDC-modeled yield and greenhouse gas emissions for a rice field under baseline and alternative management conditions in California in 1996

Management scenario	*Baseline*	*Alternative 1**	*Alternative 2***	*Unit*
Rice yield	4908	4908	4905	kg dry matter ha^{-1} year^{-1}
N_2O emission	0.1	0.2	0.1	kg N ha^{-1} year^{-1}
CH_4 emission	327	129	105	kg C ha^{-1} year^{-1}
CO_2 emission	-705	-793	-78	kg C ha^{-1} year^{-1}
Net GWP	6622	791	2706	kg CO_2-equivalent ha^{-1} year^{-1}

* Alternative 1: with straw incorporation but no winter flood; ** Alternative 2: with winter flood but no straw incorporation.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Table 6. Input parameters for simulating long-term (1930-2080) SOC dynamics in a crop field in Heilongjiang Province, China

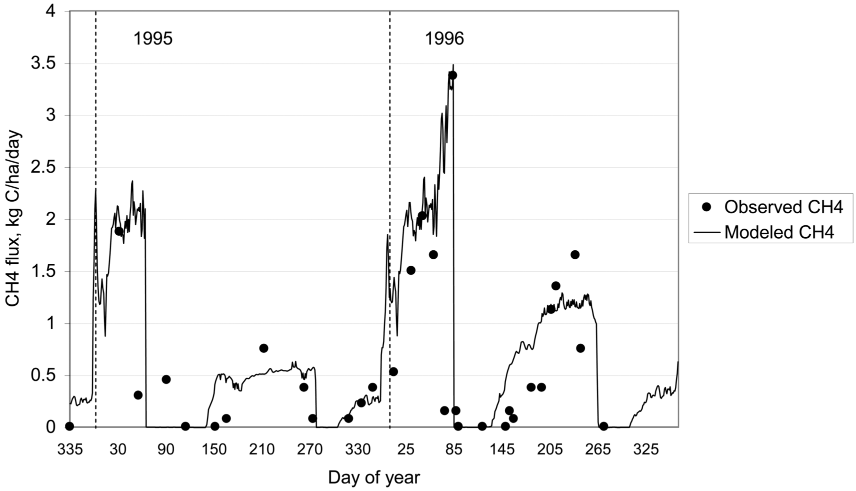
Year	*Max. yield*	*Manure application*	*Synthetic fertilizer use*	*Incorporation % of above-ground residue*	
	(kg C/ha)	*(kg N/ha)*	*(kg N/ha)*	*Baseline*	*Alternative*
1930-1940	500	20	0	0	0
1941-1950	600	30	0	0	0
1951-1960	800	40	0	0	0
1961-1970	1200	40	10	0	0
1971-1980	2000	40	40	0	0
1981-1990	2500	30	70	0	0
1991-2000	3500	0	120	0	0
2001-2010	4000	0	160	0	0
2011-2080	4500	0	180	0	50

Case Study 3: Increasing C Sequestration with Crop Residue Incorporation in a Cropland in China

Most of the agricultural fields in Heilongjiang, a major food-producing province in Northeast China, were cultivated in the 1930s by converting the original meadows or wetlands into croplands. Based on historical records, the SOC contents in the soils dramatically decreased from 6% in the 1930s to about 2% at present. Corn has been being the major crop planted in the region for decades. Corn produces a relatively large amount of residue. However, due to the lack of coal or other fuel sources, the local farmers had to utilize the crop residues as a major energy source during a quite long historical period (1930-1980). In the region, it was not uncommon to see almost 100% of the crop residues (including roots) were collected from the fields by the farmers after harvest. Farmyard manure used to be the only source of nutrients for the crops in China before the 1960s. However, the manure use was gradually abounded during the middle of the 20th century as synthetic fertilizers became available for the farmers. Since the crop residue and manure were the sole C input sources for the agricultural soils, the management on residue or manure inherently affected the SOC dynamics in the region. Only during the past about a decade, a campaign was launched in China to encourage the farmers to incorporate more crop residue to the soils. DNDC was utilized to simulate the long-term impacts of the evolving residue/manure management practices on SOC dynamics in the region.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Observed and DNDC-modeled methane fluxes from a paddy rice field with winter flood and straw incorporation in Maxwell, California in 1994-1996



DNDC-modeled methane fluxes from a paddy rice field with alternative management practices in Maxwell, California in 1994-1996

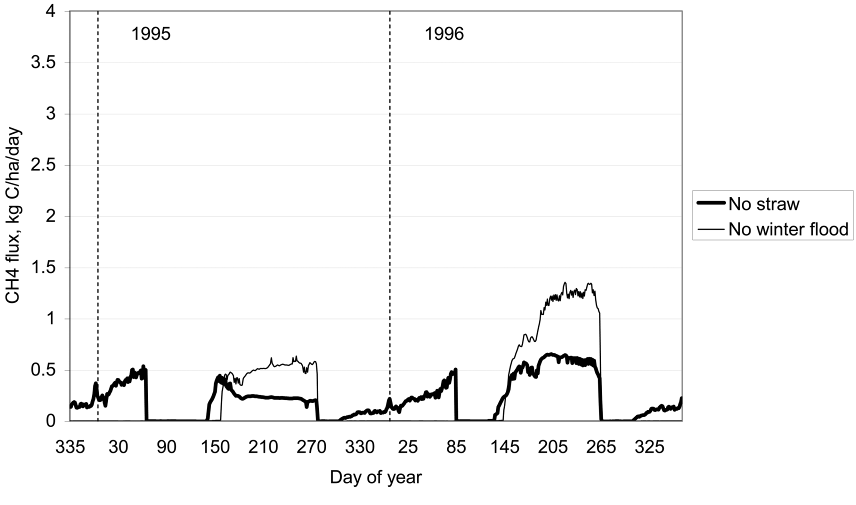


Figure 8. Modeling CH_4 emissions from a rice field in Maxwell, California. (top) Measured and modeled daily CH_4 fluxes with winter flooding and straw incorporation. (bottom) Modeled CH_4 fluxes with winter flooding but no straw incorporation and with straw incorporation but no winter flooding.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

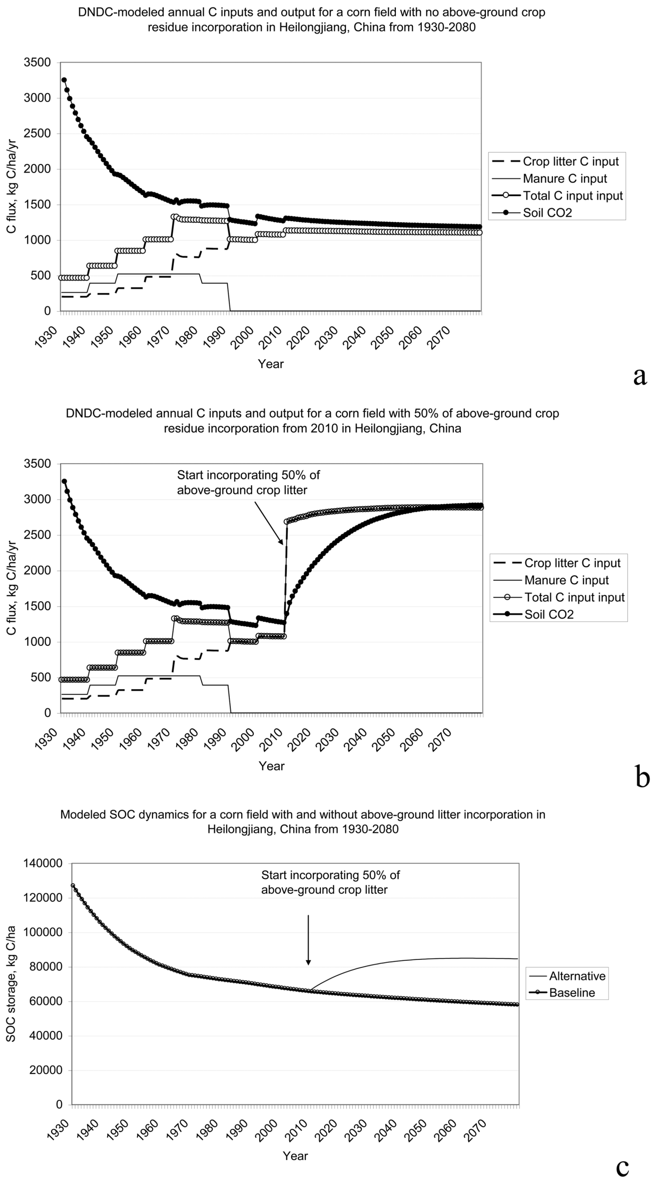


Figure 9. DNDC-simulated soil organic carbon (SOC) dynamics controlled by the SOC gain from residue and manure incorporation and the SOC loss induced by microbial respiration for a corn field in Northeast China from 1930-2080. Under the baseline conditions, soil microbial respiration rates (red line) exceeded the SOC gain rates (blue line) that caused continuous decreases in the SOC content (a). If 50% of above-ground crop residue is incorporated since 2010, the SOC gain will overwhelm the microbial respiration (b) and reverse the SOC change trend (c) in the future 60 years.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

A 150-year scenario was composed to reflect the historic changes in agricultural management practices in 1930-2000 as well as the future optional practices in 2001-2080 for the region. In the scenario, corn was continuously planted across the 150 years although its yields gradually increased. Other cropping practices such as tillage, fertilization, residue management for the period of 1930-2010 were estimated based on publications or our best knowledge. After 2010, the scenario was split to two options: continuing the zero residue incorporation or incorporating 50% of the above-ground crop residue into the soil. The daily climate data of 2000 were repeatedly utilized to serve the 150-year simulations to eliminate the effects of possible climate change on the modeled results. The management practices adopted for the long-term simulations are chronologically listed in Table 6.

Results from the baseline simulation indicated that (1) SOC content in the corn field dramatically decreased during the first 4-5 decades of the cultivation history due to the high microbial heterotrophic respiration rates and the low organic matter return; (2) the SOC decreasing trend continued but with moderate rates during 1970-2010 due to the decreased soil respiration rates; and (3) the rates of soil microbial respiration and organic matter input approached to a balance after 2010 (Figure 9a and 9c). To mimic the new policy launched in the 2000s to encourage the Chinese farmers to have more crop residue incorporated in the agricultural soils, we reran DNDC with the 150-year baseline scenario but with 50% of above-ground residue added into the soil for the period of 2010-2080. The results from the new simulation indicated that (1) the C input rates exceeded the soil CO_2 emission rate after 2010 that led to accumulation of SOC; (2) the soil heterotrophic respiration-induced CO_2 emission rates gradually increased along with increase in the SOC content; and (3) the SOC content reached to equilibrium around 2060 due to the balance between the SOC gain through the residue incorporation and the SOC loss driven the soil microbial heterotrophic respiration (Figure 9b and 9c). The modeled data indicated that the soil could sequester about 27 tons C/ha during 2010-2060 if the new residue management policy succeeds (Figure 9c).

The above-described three cases delivered a clear message that the impacts of farming management alternatives on CO_2, N_2O or CH_4 emissions can be quantified with process-based biogeochemistry models, which will enable the farmers or policy makers to assess the best management practices in a broad context of climate, soil, vegetation and management regimes.

Recommendations for Field Measurement

Modeling applications must built upon solid datasets obtained from field observations. However, most field GHG measurements are time-consuming and expensive. To meet the demand for model calibration and validation, the efficiency of GHG measurements could be elevated by setting the bottom-line methods.

For N_2O measurement, if you don't have the expensive automated chamber systems, you can use the static chambers but setting a high sampling frequency (once a day) for 3-5 days following the events of rainfall, irrigation, fertilization,

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

or soil thaw. For CH_4 measurement, statistic chamber method with sampling once a week is good enough. However, you will need to have your chambers high enough to cover the plants as the majority of CH_4 fluxes could be emitted through the plants. For quantifying soil C sequestration, if your experiments last for only a few years, you may not expect to detect the SOC change by simply measuring the SOC contents in the soil samples. In stead, measuring crop litter biomass as well as soil heterotrophic respiration could provide decent data to estimate seasonal soil C sequestration rate. To measure the soil heterotrophic respiration-induced CO_2 fluxes, you can leave a small piece of the land without seeding when you start planting your crops, and the soil heterotrophic CO_2 fluxes can be measured on the crop-blank soil as the roots have been excluded from the soil. The data obtained with the above-described methods will provide essential GHG flux data to support the model calibration and validation in the lowest cost. Of course, other methods such as eddy covariance or aerial approaches are still very useful to provide gas flux information from extended footprints for model tests at field or landscape scales. The utilization of biogeochemical models will help to design all the field measurements.

Concluding Remarks

In 1993 when “Biosphere 2”, the most glamorous artificial ecosystem built in the desert of Arizona, ended its first mission with unexpected gas concentrations found in the closed chamber, many blamed the failure on insufficient understanding of microbes. Now we are dealing with the microbes again but in “Biosphere 1”, our sole Earth’s ecosystems. Differing from the researchers of “Biosphere 2”, we now have biogeochemical models that have been substantially improved during the past two decades. By including the basic laws of physics, chemistry and biology, the biogeochemical models such as DNDC have become capable of simulating microbial activities guided by the principles of thermodynamics and reaction kinetics. However, there are still many links missing between the ecological drivers (e.g., climate, soil, vegetation and management practices) and the microbe-mediated GHG emissions. New researches with gene and isotope techniques are being launched in the U.S. and other parts of the world. Biogeochemistry, as a scientific discipline initiated about a century ago, is gaining new vigor from the rapidly increased new data and new findings. Built upon the biogeochemical concepts, biogeochemical models provide a decent platform to absorb the new observations and link them to the well established, classical sciences. Equipped with the modeling approach, may the ecosystems on the planet become not so somplex any more for our understanding.

Acknowledgments

The author thanks H. Flessa and his colleagues for their kindness to provide the N_2O datasets measured in Scheyern, Germany as well as E. Holst and his colleagues to provide the CH_4 datasets measured in Maxwell, California through relevant collaborative projects. This study was supported by NASA

NRA/Research Opportunity in Space and Earth Sciences (Grant number NNX09AQ36G, PI: Changsheng Li) and DOE/Office of Science's project "Genes, isotopes and ecosystem biogeochemistry: Dissecting methane flux at the leading edge of global change" (PI: Scott Saleska).

References

1. Li, C. Quantifying greenhouse gas emissions from soils: Scientific basis and modeling approach. *Soil Sci. Plant Nutr.* **2007**, *53*, 344–352.
2. Li, C.; Frolking, S.; Xiao, X.; Moore, B., III; Boles, S.; Qiu, J.; Huang, Y.; Salas, W.; Sass, R. Modeling impacts of farming management alternatives on CO_2, CH_4, and N_2O emissions: A case study for water management of rice agriculture of China. *Global Biogeochem. Cycles* **2005**, *19*, GB3002–GB3015.
3. Li, C.; Frolking, S.; Frolking, T. A. A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity. *J. Geophys. Res.* **1992**, *97*, 9759–9776.
4. EPA (United States Environmental Protection Agency), Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-1994. EPA-230-R-96-006, Washinton DC, 1995; p 68.
5. Vernadsky, V. I. *Problems of Biogeochemistry, the Fundamental Matter-Energy Difference Between the Living and the Inert Natural Bodies of the Biosphere*; Connecticut Academy of Arts and Sciences: New Haven, CT, 1944.
6. Li, C. Biogeochemical concepts and methodologies: Development of the DNDC model; *Quaternary Sciences* **2001**, 21, 89−99 (in Chinese with English abstract).
7. Stumm W.; Morgan, J. J. Oxidation and Reduction. *In Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 2nd ed.; Stumm, W., Morgan, J. J., Eds.; John Wiley & Sons: New York, 1981; pp 418–503.
8. Paul E. A.; Clark, F. E. Dynamics of residue decomposition and soil organic matter turnover. *In Soil Microbiology and Biochemistry*, 2nd ed; Paul, E. A., Clark, F. E., Eds.; Academic Press: San Diego, CA, 1989; pp 157–166.
9. Butterbach-Bahl, K.; Stange, F.; Papen, H.; Li, C. Regional inventory of nitric oxide and nitrous oxide emissions for forest soils of southeast Germany using the biogeochemical model PnET-N-DNDC. *J. Geophys. Res.* **2001**, *106*, 34155–34166.
10. Brown, L.; Syed, B.; Jarvis, S. C. Development and application of a mechanistic model to estimate emission of nitrous oxide from UK agriculture. *Atmos. Environ.* **2002**, *36*, 917–928.
11. Cai, Z.; Sawamoto, T.; Li, C. Field validation of the DNDC model for greenhouse gas emission in East Asian cropping systems. *Global Biogeochem. Cycles* **2003**, *17*, 1107–1116.
12. Saggar S.; Andrew, R. M.; Tate, K. R.; Hedley, C. B.; Townsend, J. A., Simulation of nitrous oxide emissions from New Zealand dairy-grazed

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

pastures and its mitigation strategies. *Proc. of the 3rd International Methane and Nitrous Oxide Mitigation Conference*, 17–21 November 2003, Beijing, China; pp. 461–468.

13. Xu-Ri, X.; Wang, M.; Wang, Y. Using a modified DNDC model to estimate N_2O fluxes from semi-arid grassland in China. *Soil Biol. Biochem.* **2003**, *35*, 615–620.
14. Grant, B.; Smith, W. N.; Desjardins, R.; Lemkc, R.; Li, C. Estimated N_2O and CO_2 emissions as influenced by agricultural practices in Canada. *Clim. Change* **2004**, *65*, 315–332.
15. Kiese, R.; Li, C.; Hilbert, D.; Papen, H.; Butterbach-Bahl, K. Regional application of PnET-N-DNDC for estimating the N_2O source strength of tropical rainforests in the Wet Tropics of Australia. *Global Change Biol.* **2005**, *11*, 128–144.
16. Pathak, H.; Li, C.; Wassmann, R. Greenhouse gas emissions from Indian rice fields: calibration and upscaling using the DNDC model. *Biogeosciences* **2005**, *2*, 113–123.
17. Jagadeesh Babu, Y.; Li, C.; Frolking, S.; Nayak, D. R.; Adhya, T. K. Field validation of DNDC model for methane and nitrous oxide emissions from rice-based production systems of India. *Nutr. Cycling Agroecosyst.* **2006**, *74*, 157–174.
18. Zhang, F.; Li, C.; Wang, Z.; Wu, H. Modeling impacts of management alternatives on soil carbon storage of farmland in Northwest China. *Biogeosciences* **2006**, *3*, 451–466.
19. Beheydt, D.; Boeckx, P.; Sleutel, S.; Li, C.; Van Cleemput, O. Validation of DNDC for 22 long-term N_2O field emission measurements. *Atmos. Environ.* **2007**, *41*, 6196–6211.
20. Smith, W. N.; Grant, B. B.; Desjardins, R. L.; Rochette, P.; Drury, C. F.; Li, C. Evaluation of two process-based models to estimate N_2O emissions in Eastern Canada. *Can. J. Soil Sci.* **2008**, *15*, 31–51.
21. Kurbatova, J.; Li, C.; Varlagin, A.; Xiao, X.; Vygodskaya, N. Modeling carbon dynamics in two adjacent spruce forests with different soil conditions in Russia. *Biogeosciences* **2008**, *5*, 969–980.
22. Fumoto, T.; Kobayashi, K.; Li, C.; Yagi, K.; Hasegawa, T. 2008. Revising a process-based biogeochemistry model (DNDC) to simulate methane emission from rice paddy fields under various residue management and fertilizer regimes. *Global Change Biol.* **2008**, *14*, 382–402.
23. Hastings, A. F.; Wattenbach, M.; Eugster, W.; Li, C.; Buchmann, N.; Smith, P. Uncertainty propagation in soil greenhouse gas emission models: An experiment using the DNDC model and at Oensingen cropland site. *Agric., Ecosyst. Environ.* **2010**, *136*, 97–110.
24. Giltrap, D. L.; Li, C.; Saggar, S DNDC: A process-based model of greenhouse gas fluxes from agricultural soils. *Agric., Ecosyst. Environ.* **2010**, *136*, 292–230.
25. Smith, W. N.; Grant, B. B.; Desjardins, R. L.; Worth, D.; Li, C.; Boles, S. H.; Huffman, E. C. A tool to link agricultural activity data with the DNDC model to estimate GHG emission factors in Canada. *Agric., Ecosyst. Environ.* **2010**, *136*, 301–309.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

26. Kesik, M.; Ambus, P.; Baritz, P. Inventories of N_2O and NO emissions from European forest soils. *Biogeosciences* **2005**, *2*, 353–375.
27. Flessa, H.; Dorsch, P.; Beese, F. Seasonal variation of N_2O and CH_4 fluxes in differently managed arable soils in southern Germany. *J. Geophys. Res., [Atmos.]* **1995**, *100*, 23115–23124.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch016

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

Chapter 17

Soil Organic Matter Cycling and Greenhouse Gas Accounting Methodologies

S. J. Del Grosso,*,[1,2] S. M. Ogle, and W. J. Parton[2]

[1]USDA, Agricultural Research Service, 2150 Centre Ave, Bldg. D, Ste. 100, Fort Collins, CO 80526
[2]Natural Resource Ecology Laboratory, Colorado State University, 1231 East Drive, Fort Collins, CO 80526
***E-mail: Steve.delgrosso@ars.usda.gov**

Soil organic matter (SOM) transformations play an important role in regulating the atmospheric concentrations of the three primary biogenic greenhouse gases (GHG), methane (CH_4), nitrous oxide (N_2O) and carbon dioxide (CO_2). Soils are a source and sink of CH_4 and CO_2, but are usually only a source for N_2O. Decomposition of SOM under anaerobic conditions leads to CH_4 emissions while aerobic decomposition results in CO_2 emissions. The microbial processes that result in N_2O emissions involve transformations of inorganic nitrogen (N) that are coupled with SOM cycling. Different methodologies of varying complexity are used to quantify these transformations and associated GHG emissions. Simple methods use regression equations that relate land management practices to GHG emissions. For example, Tier 1 Intergovernmental Panel on Climate Change (IPCC, 12) methodology uses default emission factors and activity data on N inputs, general land use and climate categories to calculate GHG emissions. Tier 2 methodology uses country or region-specific emission factors and more detailed activity data. Tier 3 methodology involves more complex process-based models that simulate the plant-soil-atmosphere system. The United States uses a Tier 3 approach to estimate soil CO_2 and N_2O fluxes from most agricultural lands for its national inventory while most other nations use Tier 1 approaches. Although higher tier approaches appear to give better estimates, uncertainty is large

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

and improvements in model algorithms and activity data are required to more reliably account the soil GHG emissions reported in national inventories.

Introduction

Soil organic matter (SOM) transformations are a major source of nutrients in soil and important gaseous compounds in the atmosphere. Annually, the decomposition of plant residues and SOM adds approximately 10 times more CO_2 to the atmosphere than fossil fuel and industrial sources (*1*). This large CO_2 source is balanced by a roughly equivalent amount of uptake by photosynthesis. Decomposition of SOM under anaerobic conditions is a leading source of atmospheric CH_4 while oxidation of atmospheric CH_4 by microbes in aerobic soils is an important sink. Soil microbial activity involving nitrogen (N) transformations results in release of N_2O, another important biogenic greenhouse gas (GHG). It is important to better understand the processes that control SOM transformations because small changes in these rates could have large impacts on atmospheric concentrations of CO_2, CH_4, N_2O, soil C storage, and N cycling rates. In this chapter, we explain the soil organic matter transformations that influence GHG concentrations, how these transformations are quantified, and methods used to account GHG fluxes at regional and greater scales.

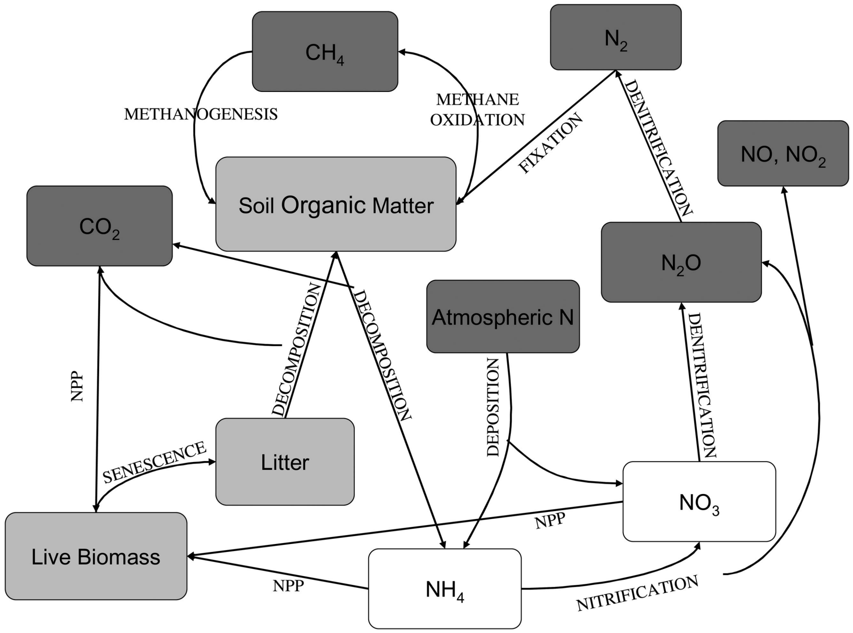

CH4
N2
METHANOGENESIS
METHANE OXIDATION
FIXATION
DENITRIFICATION
NO, NO2
Soil Organic Matter
CO2
N2O
DECOMPOSITION
DECOMPOSITION
Atmospheric N
DENITRIFICATION
NPP
DEPOSITION
SENESCENCE
Litter
NO3
NPP
Live Biomass
NPP
NH4
NITRIFICATION

Figure 1. Flow diagram of soil organic matter transformations. Fixation includes symbiotic and non-symbiotic N fixation.

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

Soil Organic Matter Cycling

Soil organic matter transformations involve immobilizing and mineralizing nutrients and carbon (C). Plants and microbes immobilize nutrients and C when they assimilate mineral compounds into organic matter; nutrients and C are mineralized when biological and chemical processes decompose organic matter and release compounds in the mineral form. The major processes involved in SOM cycling are net primary productivity (NPP), biomass senescence, decomposition of senesced pant litter and SOM, nitrification, denitrification, methanogenesis, and methane oxidation (Figure 1). The following sections describe these processes and how they are quantified.

Net Primary Productivity and Senescence

It is important to consider net primary productivity (NPP) because it provides the raw material (senesced biomass) that is converted to SOM upon decomposition. In addition to fixing atmospheric CO_2, NPP assimilates mineral N (NH_4, NO_3) from the soil (Figure 1) and thus influences the supply of nutrients available for soil microbial processes. Instead of directly measuring CO_2 assimilation, NPP is usually quantified by measuring the biomass produced during the growing season at small scales (e.g. plot level). But in addition to NPP, the biomass pool is also influenced by herbivory so assumptions must be made to infer NPP. Estimating below ground NPP is even more problematic because destructive sampling is required and it is difficult to entirely separate roots from microbes that feed on them. Analogous to the above ground situation, only biomass is measured, herbivory and root exudates are discounted, thus assumptions must be made to estimate NPP. Major controls on NPP are temperature, water status, nutrient availability, and disturbance regime (*2*). As temperature and water stress are alleviated, nutrients cycle faster and NPP increases. Disturbance events, such as fire, can increase or decrease NPP. Fire quickly mineralizes nutrients and can increase NPP in the short term (*3*). However, systems that are subject to high fire frequency tend to have lower NPP in the long run than less disturbed systems because some of the nutrients mineralized during fire events are lost from the plant-soil system via volatilization and leaching (*2*).

Decomposition

Decomposition of plant litter and SOM results in the mineralization of C which is released as CO_2 and, depending on the nutrient concentration of the material being decomposed, mineralization or immobilization of soil nutrients (Figure 1). Plant litter, except for that from legumes, typically has a low N content so decomposers must immobilize N from the mineral soil pool leading to net immobilization of nutrients during this phase of decomposition. Once litter has passed through or been incorporated into microbial biomass it is referred to as SOM. Soil organic matter has higher N concentration than litter so further decomposition results in release of N to the soil mineral N pool and net mineralization of N. Potential decomposition and net mineralization rates

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

can be measured using controlled incubations. Rates measured in this manner are considered potentials because environmental conditions are controlled and growing vegetation is not present to compete for nutrients. Buried litter bags *in situ* that are sampled through time are subject to ambient environmental conditions and are used to quantify decomposition and net nutrient mineralization rates using the principle of mass balance. Recent analysis showed that lignin content, lignin to N ratio, and environmental conditions explained the majority of variability in net mineralization and decomposition rates for buried leaf litter in various global biomes (*4*, *5*). SOM decomposition rates can also be inferred from measurements of soil CO_2 emissions but this is confounded with autotrophic respiration, unless measurements are taken from fallow soils or when plants are not active.

Nitrification and Denitrification

Nitrification is the aerobic oxidation of ammonium (NH_4) to NO_3 where N_2O, NO, and NO_2 are produced as intermediate species (Figure 1). Major controls are soil O_2 status, water content, temperature, and NH_4 availability. Most nitrified NH_4 is converted to NO_3, with the portion lost as N_2O gas less than 10%, but this fraction varies considerably based on O_2 availability and other factors (*6*). Denitrification is the anaerobic reduction of NO_3 to N_2O and N_2 (Figure 1). Major controls are soil O_2 status, water content, temperature, NO_3, and labile C availability (most denitrifiers are heterotrophs). The majority of denitrified NO_3-N can be emitted as N_2O or N_2. As conditions become more anaerobic and the supply of electron donor (labile C) relative to initial electron acceptor (NO_3) increases, the portion of N_2 relative to N_2O emitted also increases (*7*). Nitrification and denitrification rates can be measured reliably for incubation studies. But in field situations, often soil N_2O flux measurements are the only indicator of nitrification and denitrification rates and N_2O from nitrification cannot be distinguished from N_2O from denitrification. Furthermore, it is difficult to accurately quantify N_2O emissions rates in the field because they are highly variable in space and time and often respond non-linearly to the key drivers. Methods used to estimate soil gas fluxes to the atmosphere can be divided into two broad classes known as bottom up and top down approaches. Bottom up approaches calculate soil surface gas flux rates using ground based chambers that trap gases emitted from the soil surface while top down approaches infer gas flux based on changes in the atmospheric concentration of gases in space or time. Theses methods are describes in detail in Chapter 1 of this volume.

Methanogenesis and Methane Oxidation

Methanogenesis is a form of anaerobic respiration, often representing the final step in the decay of organic matter, where the terminal electron acceptor is carbon compound such as acetic acid (C_3COOH) or CO_2 (Figure 1). Controls on methane production include O_2 status, temperature, pH, and C availability (*8*, *9*), while CH_4 emissions from soil is also influenced by gas diffusivity and plant species, as plant transport is often the dominant pathway for soil CH_4 emissions. Oxidation of atmospheric methane, as well as methane created in deeper soil layers, is carried out by methanotrophic bacteria in aerated surface soil layers (Figure 1). Major controls are soil gas diffusivity, temperature, and CH_4 availability (*10*). Both methanogenesis and methane oxidation likely occur in most soils. In drained, upland soils, methane oxidation dominates and these soils are net CH_4 sinks, while in low lying, saturated soils methanogenesis dominates and these soils are net sources. As with N_2O, both ground based chambers and top down methods are used to measure CH_4 fluxes from soils.

Methods used to measure the rates of soil organic matter transformations are not perfect because usually only pool sizes can be directly measured and rates must be inferred. Field sampling of vegetation and soil processes using bottom up methods requires varying degrees of disturbance of the plant-soil system. Top down methods require little, if any, disturbance, but sample across large areas so rates of processes occurring at small scales are confounded. Also, more than one process often influences what is measured. For example, both nitrification and denitrification contribute to measured N_2O fluxes. Consequently, models are often used to estimate rates of these processes. Models have advantages of not requiring disturbance and simulating flows of material for different process (e.g., NPP, N gas fluxes for nitrification and denitrification individually) as well as pool sizes (e.g., standing biomass, soil organic carbon). However, models are limited in that they are simplifications of reality and are constrained by measurements, which themselves are imperfect. One reason it is difficult to model soil processes is that the controlling factors interact in different ways. For example, heavy livestock grazing is expected to increase mineral N availability in soil, and hence N_2O emissions. But in arid temperate grasslands, grazing can decrease snow retention (and thus soil water content) due to reduced vegetation cover such that N_2O emissions during the spring thaw period can be greatly reduced compared to ungrazed systems (*11*, *12*).

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

GHG Accounting Methodologies

Because it is not feasible to measure GHG emissions from different sources at regional and larger scales, methodologies involving models of varying complexity have been developed. We discuss these methodologies in the context of national greenhouse gas inventories. Signatory nations of the United Nations Framework Convention on Climate Change (UNFCCC) agree to report their national GHG emissions annually to the UNFCCC using agreed upon accounting methodologies developed by the Intergovernmental Panel on Climate Change (IPCC). The IPCC Good Practice Guidelines define three methodological Tiers for calculating GHG emissions for national inventories (*13*). Tier 1 methods are the easiest to use and employ default emission factors and country specific activity data to estimate emissions. Emission factors define GHG emissions per unit of agricultural activity; e.g., 1 kg N_2O-N is emitted directly from soils for every 100 kg of N fertilizer added (Figure 2). Tier 2 methods use the same approach as Tier 1 but apply country or region specific emission factors and require more disaggregated activity data. Tier 3 methods use process-based simulation models and/or inventory monitoring systems (e.g., (*14*, *15*)). In addition to soil C stock changes, and direct soil N_2O and CH_4 emissions, the IPCC Guidelines recommend accounting for indirect N_2O emissions (*13*). Indirect N_2O results from N that left the agricultural system in a form other than N_2O (e.g., gaseous NO_x and NH_3, dissolved NO_3 leached into ground water) and converted to N_2O offsite (Figure 2).

The IPCC Guidelines recommend including estimates of uncertainty and prescribe how to combine different sources of uncertainty (*13*). Tier 1 methods usually have large uncertainty; e.g., the 95% confidence interval (CI) for direct N_2O emissions from N additions to soils ranges from 0.3 to 3.0 kg N_2O-N for every 100 kg of N fertilizer added. Tier 2 methods have lower uncertainty because country specific emissions factors that better reflect region specific cropping practices and environmental conditions are used. Tier 3 methods should provide the most certain estimates because they use complex models that account for more of the variables that influence emissions and how they interact. Although Tier 3 methods should yield more accurate and precise estimates, most nations use Tier 1 and 2 methods, because Tier 3 methods require extensive resources to develop and validate model outputs, acquire model input data, execute simulations, process model results, and verify quality control.

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

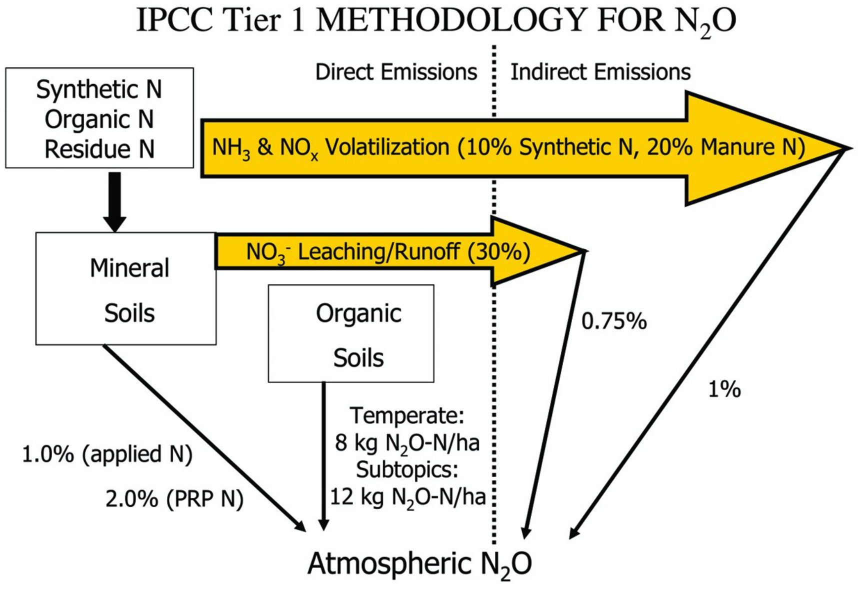

IPCC Tier 1 METHODOLOGY FOR N_2O
Direct Emissions
Indirect Emissions
Synthetic N
Organic N
Residue N
NH_3 & NO_x Volatilization (10% Synthetic N, 20% Manure N)
Mineral Soils
NO_3^- Leaching/Runoff (30%)
Organic Soils
0.75%
1%
Temperate:
8 kg N_2O-N/ha
Subtopics:
12 kg N_2O-N/ha
1.0% (applied N)
2.0% (PRP N)
Atmospheric N_2O

Figure 2. IPCC default Tier 1 methodology for soil Nitrous oxide (N_2O) emissions. PRP N refers to nitrogen deposited onto pasture, range,and paddock soils by grazing animals (unmanaged livestock waste). In contrast, manure N refers to N in managed livestock waste that was applied to cropped or grazed fields by humans.

IPCC Tier Comparison for Soil Carbon Stock Changes

Soil organic carbon stock changes in U.S.A. croplands are estimated annually as part of the National Greenhouse Gas Inventory (*16*). The methods have been refined over time from the simplest Tier 1 method to the most complex Tier 3 method, providing an example of how estimates and uncertainties change with application of different methodological tiers. For this comparison, the Tier 1 method used the default factors and equations from the 2006 IPCC Guidelines (*13*), the Tier 2 method was developed using the same equations with country specific factors (*17*, *18*), and the Tier 3 method was based on estimating the carbon stock changes with a process-based simulation model (*14*). All three methods were implemented with activity data from the 1997 USDA National Resource Inventory (*19*, *20*). The Tier 3 method has been customized for the crop management conditions in the US, and thus incorporated additional activity data about the production systems compared to the Tier 1 and 2 methods. For example, the Tier 3 method requires additional data on fertilization rates and management practices such as planting and harvesting dates (*16*).

The estimated changes in soil organic C stocks in 1997 were not statistically different among the three approaches (Figure 3), suggesting that the methods provide comparable estimates for the change in soil organic C stocks. The major difference between the methods was level of precision in the result. The confidence intervals had ranges of ±59%, ±40% and ±16%, for the Tier 1, 2 and 3 methods, respectively. The Tier 2 method increases the precision by 19%, while the Tier 3 increases the precision by another 24%. Note that this comparison does not include complete coverage of all the cropped land in the US because the Tier 3 method was not applied to all cropped soils, as explained in the next section.

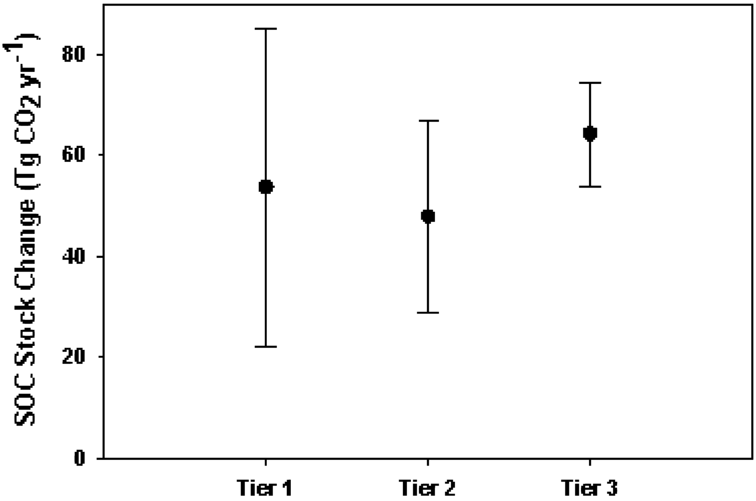


Figure 3. Soil organic C stock change (Tg CO_2 yr^{-1}) in 1997 for US croplands using IPCC Tier 1, 2 and 3 methods.

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

One of the key goals for developing higher Tier methods within the IPCC guidance (*13*) is to reduce uncertainties in the estimated greenhouse gas emissions. The example for US croplands is consistent with this goal in terms of increasing the precision in the estimated soil organic C stock change for US croplands. It is not surprising that the estimates are relatively consistent among the methods, particularly the Tier 1 and 2 methods because a large portion of the data used to derive IPCC default factors is from experiments conducted in the US (*21*). The Tier 3 method addressed practices with more specificity which led to a higher estimated change in soil organic C stocks, but again this result has a large overlap with lower tier results. Therefore, developing country specific-factors with Tier 2 and addressing crop management with greater specificity in the Tier 3 method appears to have a larger influence on the precision of the estimate than the accuracy, assuming that the confidence intervals contain the true value of soil organic C stock change. More comparative analyses among estimates from different tiers will be needed to determine if this result is generalizable.

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

U.S.A. Soil GHG Inventory

The U.S.A. uses a combination of Tier 1, Tier 2, and Tier 3 approaches to estimate nationwide GHG emissions from agricultural soils (*16*). A Tier 3 approach is used to estimate soil C stock changes for major cropping systems (corn, soybean, wheat, hay, sorghum, cotton) and non-federally managed grasslands used for livestock grazing (*14*). Specifically, the CENTURY ecosystem model simulates cropped and grazed systems across the U.S.A. at small spatial scales (sub county) using data from the National Resources Inventory (*19*, *20*). A Tier Two approach is used for soil C stock changes for minor crops, organic soils, and federal grasslands (*17*, *18*). Similarly, a Tier 3 method using the DayCent ecosystem model is used to calculate N_2O emissions for major cropping systems and non-federally managed grasslands used for livestock grazing (*15*). A Tier 1 approach is used to estimate N_2O emissions from minor crops, cropped and grazed organic soils, and federal grasslands, as well as CH_4 emissions from flooded rice paddies (*16*).

For both soil C stock changes and N_2O emissions calculated using the Tier 3 approaches based on CENTURY and DayCent model simulations, a Monte Carlo method is used to quantify uncertainty in model outputs (*14*, *15*). Repeated simulations, using random draws from probability distribution functions, quantify uncertainty for key model inputs that are not precisely known, and empirical based estimators derived from comparing model outputs with measured values are used to quantify uncertainty due to model algorithms and parameterizations being imperfect representations of reality. IPCC (*13*) Guidelines are used to quantify uncertainty for the Tier 1 and 2 estimates and to combine uncertainties into an overall uncertainty range for each GHG source category.

Nitrous oxide emissions account for the vast majority of soil emissions in the U.S.A. because other key soil emissions, such as CH_4 from rice paddies, are small because rice paddies are a small portion of total agricultural land and agricultural soils are a net CO_2 sink (*16*). In 2008, cropped soils were an N_2O source of 154

Tg CO_2 eq. with a 95% CI of -26% to +57%; grazed soils were an N_2O source of 62 Tg CO_2 eq. with a 95% CI of -37% to +153% (*22*). Agricultural soils were estimated to be a small source of CH_4 (8 Tg CO_2 eq. with a 95% CI of -57% to +127%) and a sink for CO_2 of 40 Tg CO_2 eq. with a 95% CI of -53% to +42%. In aggregate, agricultural soils are estimated to be a GHG source of 184 Tg CO_2-C eq. yr-1 with a 95% confidence interval of -19 to +37% (*22*).

Conclusion

Soil organic matter cycling results in both release and uptake of the three important biogenic GHG's (CO_2, CH_4, N_2O). Because such vast amounts of C and N are cycled through soils, small changes in the amounts of these elements cycled, or in the portions of cycled C and N that are converted to GHG's, can result in substantial changes in the atmospheric concentrations of these gases. In recent years, both measuring and modeling methods used to quantify SOM cycling and the associated GHG fluxes have improved, leading to narrowing of confidence intervals for estimates of the rates of these processes and the associated gas fluxes. Still, the uncertainties remain large compared to other sources of anthropogenic GHG's (e.g. fossil fuel combustion). Availability of more observational data collected at various spatial and temporal scales and continued improvement of modeling methods should result in further increases in the accuracy and precision of GHG flux estimates resulting from SOM transformations.

References

1. Houghton, R. A. The contemporary carbon cycle. In *Biogeochemistry*; Schlesinger, W. F., Ed., Elsevier Science: Amsterdam, 2005; pp 473–513.
2. Del Grosso, S. J.; Parton, W. J.; Stohlgren, T. S.; Zheng, D.; Bachelet, D.; Hibbard, K.; Olson, R.; Prince, S. Global net primary production predicted from vegetation class, precipitation and temperature. *Ecology* **2008**, *89*, 2117–2126.
3. Seastedt, T. R.; Knapp, A. K. Consequences of Nonequilibrium Resource Availability Across Multiple Time Scales: The Transient Maxima Hypothesis. *Am. Nat.* **1993**, *141*, 621–633.
4. Adair, E. C.; Parton, W. J.; Del Grosso, S. J.; Silver, W. L.; Harmon, M. E.; Hall, S. A.; Burke, I. C.; Hart, S. C. Simple three-pool model accurately describes patterns of long-term litter decomposition in diverse climates. *Global Change Biol.* **2008**, *14*, 2636–2660.
5. Parton, W. J.; Silver, W. L.; Burke, I. C.; Grassens, L.; Harmon, M. E.; Currie, W. S.; King, J. Y.; Adair, E. C.; Brandt, L. A.; Hart, S. C.; Fasth, B. Global-scale similarities in nitrogen release patterns during long-term decomposition. *Science* **2007**, *315* (19), 361–364.
6. Khalil, K.; Mary, B.; Renault, P. Nitrous oxide production by nitrification and denitrification in soil aggregates as affected by O_2 concentration. *Soil Biol. Biochem.* **2004**, *39*, 687–699.

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

7. Del Grosso, S. J.; Parton, W. J.; Mosier, A. R.; Ojima, D. S.; Kulmala, A. E.; Phongpan, S. General model for N_2O and N_2 gas emissions from soils due to denitrification. *Global Biogeochem. Cycles* **2000**, *14*, 1045–1060.
8. Segers, R. Methane production and methane consumption: a review of processes underlying wetland methane fluxes. *Biogeochemistry* **1998**, *41*, 23–51.
9. Walter, B. P.; Heimann, M. A process-based, climate-sensitive model to derive methane emissions from natural wetlands: Application to five wetland sites, sensitivity to model parameters, and climate. *Global Biogeochem. Cycles* **2000**, *14* (3), 745–765.
10. Del Grosso, S. J.; Parton, W. J.; Mosier, A. R.; Ojima, D. S.; Potter, C. S.; Borken, W.; Brumme, R.; Butterbach-Bahl, K.; Crill, P. M.; Dobbie, K.; Smith, K. A. General CH_4 oxidation model and comparisons of CH_4 oxidation in natural and managed systems. *Global Biogeochem. Cycles* **2000**, *14*, 999–1019.
11. Wolf, B.; Zheng, X.; Brüggermann, N.; Chen, W.; Dannenmann, M.; Han, X.; Sutton, M. A.; Wu, H.; Yao, Z.; Butterbach-Bahl, K. Grazing-induced reduction of natural nitrous oxide release from continental steppe. *Nature* **2010**, *464*, 881–884.
12. Del Grosso, S. J. Grazing and nitrous oxide. *Nature* **2010**, *464*, 843–844.
13. IPCC. *Intergovernmental Panel on Climate Change Guidelines for National Greenhouse Gas Inventories. Volume 4: Agriculture, Forestry and Other Land Use.* Chapter 11: N_2O Emissions from Managed Soils, and CO_2 Emissions from Lime and Urea Application. 2006.
14. Ogle, S. M.; Breidt, F. J.; Easter, M.; Williams, S.; Killian, K.; Paustian, K. Scale and uncertainty in modeled soil organic carbon stock changes for US croplands using a process-based model. *Global Change Biol.* **2010**, *16*, 810–822.
15. Del Grosso, S. J.; Ogle, S. M.; Parton, W. J.; Breidt, F. J. Estimating Uncertainty in N_2O Emissions from US Cropland Soils. *Global Biogeochem. Cycles* 2010, 24, GB1009, doi:10.1029/2009GB003544.
16. EPA. *Inventory of US greenhouse gas emissions and sinks: 1990-2008.* Environmental Protection Agency, Office of Atmospheric Programs. 2010. Washington, D.C.
17. Ogle, S. M.; Eve, M. D.; Breidt, F. J.; Paustian, K. Uncertainty in estimating land use and management impacts on soil organic carbon storage for U.S. agroecosystems between 1982 and 1997. *Global Change Biol.* **2003**, *9*, 1521–1542.
18. Ogle, S. M.; Breidt, F. J.; Paustian, K. Bias and variance in model results associated with spatial scaling of measurements for parameterization in regional assessments. *Global Change Biol.* **2006**, *12*, 516–523.
19. Nusser, S. M.; Goebel, J. J. The national resources inventory: a long term monitoring programme. *Environ. Ecol. Stat.* **1997**, *4*, 181–204.
20. USDA-NRCS.. *Summary Report 1997 National Resources Inventory (revised December 2000).* United States Department of Agriculture, Natural Resources Conservation Service, Iowa State University Statistical. Laboratory. 2000. Ames, Iowa.

21. Ogle, S. M.; Breidt, F. J.; Paustian, K. Agricultural Management Impacts on Soil Organic Carbon Storage under Moist and Dry Climatic Conditions of Temperate and Tropical Regions. *Biogeochemistry* **2005**, *72*, 87–121.
22. USDA. *U.S. Agriculture and Forestry Greenhouse Gas Inventory: 1990-2008*. Del Grosso, S. J., Eve, M., Eds.; Technical bulletin in press. U.S. Department of Agriculture, Office of the Chief Economist: Washington, D.C., 2011.

Downloaded by STANFORD UNIV GREEN LIBR on June 21, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch017

Chapter 18

Emissions of Nitrous Oxide from Agriculture: Responses to Management and Climate Change

M. Abdalla,*,[1] P. Smith,[2] and M. Williams[1]

**[1]Department of Botany, School of Natural Sciences,
Trinity College Dublin, Dublin 2, Ireland
[2]School of Biological Sciences, University of Aberdeen, Cruickshank
Building, St. Machar Drive, Aberdeen, AB24 3UU, U.K.
*E-mail: abdallm@tcd.ie**

Nitrous oxide (N_2O) is a potent greenhouse gas in the atmosphere and its emissions are of great concern worldwide. This Chapter reviews the production and importance of nitrous oxide from agricultural soils and provides examples of management practices that may affect the extent of emissions from both grasslands and cereal systems. In addition, the use of geochemical models to estimate the present and future emissions of nitrous oxide is shown using DeNitrification-DeComposition (DNDC) and DayCent (Daily Century) models as working examples.

Background

Nitrous oxide (N_2O) is a potent greenhouse gas in the atmosphere and its emissions are of great concern worldwide. It has a role in global warming (*1*) and in the destruction of the stratospheric layer (*2*, *3*) with a radiative forcing of about 6% of all greenhouse gases in the atmosphere (*4*, *5*). The concentration and the annual rate of increase for N_2O are considerably less than those calculated for the two other major greenhouse gases (GHGs), carbon dioxide (CO_2) and methane (CH_4). On a kg to kg basis, N_2O has a radiative forcing of approximately 298 times that of carbon dioxide, and an atmospheric life time of about 150 years compared with a radiative forcing of approximately 20 times that of carbon dioxide and atmospheric life time of 12 years for methane (*5*, *6*). The atmospheric concentration of N_2O is increasing linearly at a rate of 0.7 ppb y^{-1} (≈ 0.3%)

with levels measured in the year 2005 at 319 ppbv (*5*). Emissions of N_2O to the atmosphere result in impacts on human health (e.g impacts on pulmonary and respiratory function of the aggravation of pre-existing disease such as asthma resulting in increase excess mortality), visibility, crop damage, and regional acidification and eutrophication (*7*), while releases to land result in eutrophication to both fresh and coastal waters. Climate change, due largely to increases atmospheric concentrations of GHGs, could also cause aggregated monetary damage of 1.5 to 2% of world gross domestic product (GDP) and 2 to 9% of national gross national product (GNP) for developing countries for a two-fold increase in atmospheric CO_2 concentration from the pre-industrial level (*8*).

Agriculture represents a considerable source of N_2O release to the atmosphere (*9*) accounting for approximately one-fifth of the annual increase in radiative forcing (*5*, *10*) and approximately 65-70% of the total N_2O produced by terrestrial ecosystems (*11*). This is equivalent to a global warming potential (GWP) of about 1.0 Pg C y^{-1} (*12*). Sources of N_2O are both natural and anthropogenic, the latter being of most concern with regard to increasing concentrations of GHG's in the atmosphere. The major part of this global flux is the N_2O produced in soils as an intermediate during nitrification and denitrification (*13*). The combined soil processes of mineralization, nitrification and denitrification convert applied organic and inorganic N-fertilizer to N_2O which then diffuses from the soil to the atmosphere. Primary reasons for enhanced N_2O emission from cultivated soils are increased N inputs by mineral fertilizers, animal wastes and biological N fixation (*10*, *14*). Nitrogen losses to the atmosphere (*15*) and to ground water by leaching are higher in intensively managed grasslands than in arable crops (*16*). The emission of N_2O from grazed grasslands contributes about 30% of the total global warming potential (*17*). This is due to nitrogen provided by fertilizers, fixed by legumes and excreted by animals.

National inventories of N_2O fluxes from agricultural soils, as required by signatory countries to the United Nations Framework Convention of Climate Change (UNFCC), are mainly derived from the use of the default IPCC Tier 1 method, i.e. emission factors (EF). Here, 0.9-1.25% of applied inorganic nitrogen to agricultural soils is assumed to be released to the atmosphere as nitrous oxide-N (*5*, *18*). This standard reporting procedure has advantages in collating annual inventories, but may mask significant variations in emission factors (EFs) on a regional scale (*14*, *18*).

Important Microbial Processes of N_2O in Soils

Nitrous oxide is produced biologically in soils mainly during nitrification (*19*) and denitrification (*20*) processes. Other processes that lead to production of N_2O are nitrifier denitrification and nitrate ammonification (Figure 1; (*21*)). All of these processes may occur simultaneously in different microsites of the same soil (*22*).

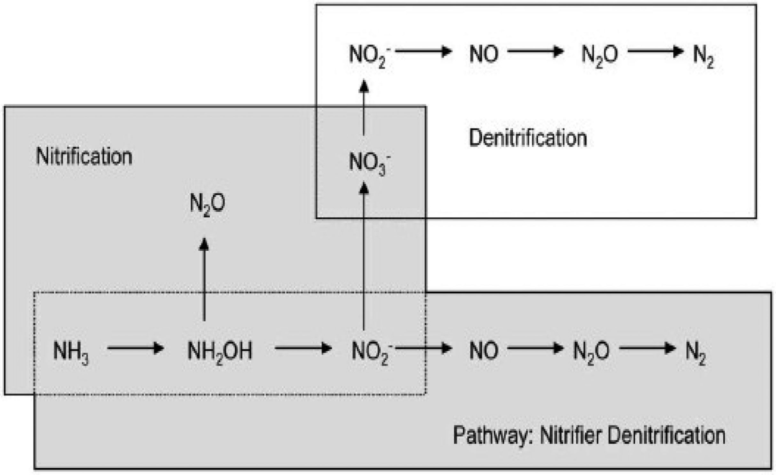

Nitrification
Denitrification
Pathway: Nitrifier Denitrification
NO_2^- → NO → N_2O → N_2
NO_3^-
N_2O
NH_3 → NH_2OH → NO_2^- → NO → N_2O → N_2

Figure 1. Nitrous oxide production from microbial processes. (Reproduced with permission from reference (21). Copyright 2001, Elsevier.)

Nitrification

Nitrification is a two-stage oxidation process in which ammonia is oxidized to nitrite (NO_2^-) and the nitrite to nitrate (NO_3^-) producing N_2O as a by-product (*23*):

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ + \text{energy} \quad (1)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{energy} \quad (2)$$

Nitrification rates are high when NH_4^+ is readily available (*24*), but the concentrations of other nutrients generally have little effect (*25*, *26*). Nitrification is generally lower at low pH, low O_2, low soil moisture content, and high litter C: N ratios (*27*). It is significant in environments where O_2 is not limiting (*28*) because many bacteria isolated from soils and sediment (e.g. *Pseudomonas*, *Aeromonas* and *Moraxella genera*) are capable of nitrate respiration in the presence of O_2 (*28*, *29*).

A variety of processes affect the concentration of NH_4^+ in the soil solution, including uptake by plants, immobilization by microbes, and fixation in clay minerals. Some of the remaining NH_4^+ may undergo nitrification, in which the oxidation of NH_4^+ to NO_3^- is coupled to the fixation of carbon by chemoautotrophic bacteria in the genera *Nitrosomonas* and *Nitrobacter* (*30*). In some cases, organic N is also oxidized by heterotrophic nitrification, producing NO_3^- (*31*). Nitrate may be taken up by the plants and microbes or lost from the ecosystem in runoff waters or in emissions of N-containing gases. Nitrate taken up by soil microbes (mobilization) is reduced to NH_4^+ by nitrate reductase and used in microbial growth (*32*). At any time the extractable quantities of NH_4^+ and NO_3^- in the soil represent the net result of all of these processes.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Denitrification

Denitrification is a microbial process in which heterotrophic facultative bacteria reduce NO_3^- to N_2O and N_2 gases under anaerobic conditions as illustrated in equation 3 (*33*). This process takes place under conditions where O_2 supply (the respiratory electron acceptor) is limited (*34*). It is often considered to be the main N_2O producing process in soils that returns N_2 to the atmosphere, completing the global biogeochemical cycle of nitrogen (*35*). Many studies have reported N_2O emissions after N application to increase with increasing soil water content and most rapidly above 60% water-filled pore space (WFPS) (*36–38*).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (3)$$

The capacity to denitrify is widely spread among a number of taxonomic and physiological groups of bacteria (*39*). However, only a few genera seem to be numerically dominant in soil, marine freshwater and sediment environments. *Pseudomonas* species capable of denitrification are dominant in many environments, with *Alcaligenes* species commonly comprising the second most numerous denitrifying populations (*39*). Denitrification is widespread in terrestrial ecosystems, especially those in which organic carbon and nitrate is readily available in the soil (*40*, *41*). Rainfall generally increases the rate of denitrification, because the diffusion of oxygen is slower in wet soils (*42*). Other factors, which have a bearing on this process, are soil pH (*43*), temperature (*20*) and soil particle distribution (*44*). These factors in turn are influenced by soil topography, climate, vegetation type, geology and the pattern of organic C production and decomposition. Moreover, in agro-ecosystems, soil management affects one or more of controlling factors of denitrification (*45*), which can either enhance or retard denitrification rates.

Main Driving Factors of N_2O

Soil Nitrogen

All forms of nitrogen input to agricultural soils, such as mineral fertilizer, organic manures, biological nitrogen fixation, green manures or post-harvest crop residues, represent potential contributory substrate for N_2O emissions. However, the amount of N_2O released to the atmosphere also depends on a complex interaction between soil properties, climatic factors and agricultural practices, the main soil factors being NH_4^+ and NO_3^- concentration (*14*, *46*, *47*), soil aeration status and soil water content (*48*), microbial activity (*49*) and finally, soil pH and soil temperature (*50*). Due to the complexity of interactions, one single factor may not always correlate with N_2O flux.

Soil Moisture

Soil moisture affects N_2O emission rate by reducing the volume of gas in the soil, restricting O_2 supply and by dissolving the applied N fertilizer. The moisture and aeration status of a soil is closely related to its physical properties, as determined mainly by soil texture, mineralogy, stoniness, organic matter content and structure, rainfall/ irrigation regime and the crop or vegetation cover. Plants consume oxygen by root respiration and use water, thereby decreasing the amount of water held in the pore spaces. Fluctuations in the water filled pore space in turn influence the rate of N_2O diffusion in the soil, the amount of N_2O dissolved in the soil water, the rate of N_2O production by soil micro-organisms, the rate of reduction of N_2O to N_2 by soil micro-organisms and the amplitude in the diurnal change in temperature that occurs at any given depth in the soil (*51*). Significant correlations between soil moisture and N_2O fluxes from soils were found from both the grass and arable lands (*14*, *20*). These suggest that the high rainfall in winter and early spring together with soil properties, such as drainage characteristics are important in the assessment of N_2O emission (*52*).

On grassland, rainfall, particularly around the time of N fertilizer application was the main driving factor for N_2O during the growing season (*53*). Therefore, seasonal changes in soil moisture have strong influences on the N_2/ N_2O ratio (*54*). Soil moisture primarily and positively regulates the spatial and seasonal variability of N_2O emissions (*55*). Soil water content and soil N availability were found co-required for high N_2O emissions from a continuous maize cropping system (*56*). Similar results have been demonstrated in forest and grassland systems (*37*, *57*).

In one experiment (*58*), the relationship between N_2O emissions and water filled pore space (WFPS) was highly significant. Here, as WFPS increases, diffusion of oxygen into soil aggregates would decrease causing an increase in N_2O production by denitrification (*58*). Flux from arable soil was noted to be 30 times greater at 80% WFPS than at 60%, while the corresponding flux from the grassland soil was about 12 times greater than its counterpart at 60% WFPS. Similar results were found by (*59*) where nitrous oxide emissions increase logarithmically between 52 and 85% WFPS. Water stimulates denitrification by temporarily reducing the oxygen diffusion into the soil as well as by increasing the solubility of organic carbon and nitrate (*35*). Prolonged water logging can limit denitrification if it also restricts nitrification which produces nitrate for denitrification. Studies both in the tropics (*60*) and in temperate climates (*36*) suggest that maximum N_2O emissions occur at WFPS of 80 - 85%. Further support for the importance of this higher range indicated that the highest fluxes were induced by the loss of macro-pores due to compaction, which increased WPFS to a mean value of 85% (*61*). This suggests that a much wetter and greater degree of anaerobicity is required to produce maximum N_2O emissions.

Soil Temperature

Temperature affects N_2O emissions by either increasing the emission rate of microbial activity, (for which the Q_{10} is the way of quantifying the increase), or due to freeze/ thawing events. Rates of nitrification and denitrification increase with increasing temperature, hence, microbial activity is highly temperature dependent (*62*, *63*). In an incubation study, we found strong correlation between soil denitrification and temperature (*20*). The calculated Q_{10} was 6 and the activation energy for denitrification was 47 KJ mol^{-1} (Figure 2). The difference in N_2O emissions from winter to summer indicates that temperature is a controlling variable. During winter N_2O emissions are positively correlated with temperature. Direct linear relationships between N_2O emission and seasonal and diurnal temperature changes have been shown for many soils in temperate climates (*62*, *63*). About 89% of diurnal variability in N_2O emissions release from decomposing grass mulch could be explained by changes in temperature (*64*). The diurnal pattern in N_2O production from arable soils was studied by (*65*), using micrometeorological techniques. The N_2O emission was found to be strongly temperature dependent with the best predictor being soil temperature at 12 cm depth. Whereas, (*66*) observed a diurnal pattern in N_2O production from grassland soils treated with slurry and ammonium nitrate fertilizer, with strong correlation between N_2O emission and temperature at 2.5-5 cm.

Warmer soil temperatures were not sufficient to enhance the emission of N_2O, but were necessary to allow the soil microbial population to respond to other perturbations such as fertilization or rainfall, and particularly a combination of the two. If soil WFPS or mineral N content are limiting, there may not be a clear relationship with temperature. However, when only those data points where the other factors are non-limiting are considered, there is evidence of a very steep response to temperature, with Q_{10} values of up to 8 (*36*). In tropical natural soils, where seasonal variations in temperature are much smaller, evidence of diurnal variations is mixed. For example, in the close canopy of a Terra Firme forest in Brazil, no diurnal variations in N_2O emissions were observed (*67*), but in a semi-deciduous forest in Venezuela daytime fluxes were typically 50% larger than night time fluxes. However, in a nearby savannah diurnal temperature changes did not affect N_2O emissions (*68*). Moreover, the N_2/ N_2O ratio was also found to increase with soil temperature (*69*).

Nitrous oxide emissions at low temperatures have shown a large temperature anomaly. Several studies have shown high N_2O fluxes at low soil temperatures in northern European and North American soils, when 38–70% of the annual emissions can take place during winter (*70–75*). The highest N_2O fluxes at low temperatures have been associated with freezing and thawing cycles (*49*, *76*, *77*). Several alternative mechanisms have been proposed to explain the high N_2O release during thawing, including the physical release of the trapped N_2O (*78*), an increase in the availability of substrates and associated denitrification activity (*79*, *80*), a combination of physical N_2O release and increased microbial activity (*49*, *81*) and chemical production of N_2O (*82*).

Effects of Management on N_2O Emissions

Application of N Fertilizer

To meet the needs of human dietary requirements, the use of synthetic nitrogen fertilizers in agriculture has increased worldwide (*83*). In 1950 global synthetic N input into soils constituted 7% of a total N input of 56 Mt, whilst in 1996 synthetic N was approximately 43% of a total N input of 190 Mt (*84*). Over this 46 year period the global input of synthetic N into soils has increased from 4 to 82 Mt and is expected to increase at an annual rate of 1.4% until 2012 (*85*). This anthropogenic input is considered equivalent to biological N fixation (*86*) and results in significantly more N_2O emissions from agricultural soils over the past 100 years (*86*).

Nitrogen enters ecosystems via two natural pathways, the relative importance of which varies greatly from ecosystem to ecosystem. The first, atmospheric deposition, accounts for approximately 5 - 10% of the usable nitrogen that enters most ecosystems. In this process, NH_4^+ and NO_3^- are added to soil by being dissolved in rain or by settling as parts of fine dust or other particulates (*87*). The other pathway for nitrogen entering ecosystems is via nitrogen fixation. Only certain prokaryotes can fix nitrogen, that is, convert N_2 into minerals that can be used to synthesize nitrogenous organic compounds such as amino acids. Nitrogen is fixed in terrestrial ecosystems by free-living (non-symbiotic) soil bacteria as well as by symbiotic bacteria in the root nodules of legumes and certain other plants. Some cyano-bacteria fix nitrogen in aquatic ecosystems. In addition to these natural sources of usable nitrogen, industrial fixation of nitrogen for fertilizer makes a major contribution to the pool of nitrogenous minerals in terrestrial and aquatic ecosystems (*87*).

N fertilizer has a direct influence on N_2O production by provision of N for both nitrification and denitrification. In a study by (*20*) the mean background N_2O-N emission from a non fertilized pasture was 1 kg ha^{-1} y^{-1} whilst, that from a fertilized pasture was 2.4 kg $ha^{-1}y^{-1}$. The highest peaks of N_2O fluxes of 67 and 38.7g N_2O-N ha^{-1} were associated with the time of application of synthetic N fertilizer (Figure 3). Here, 63% of the annual flux from grassland was associated with the period of fertilizer application. In another study using different N fertilization rates, (*14*) found that reducing fertilizer application rate by 50% reduced N_2O emissions from soils by 57% without significant effect on grain yield (at 15% moisture; Figure 4) or grain quality in terms of required protein content for two consecutive seasons. Collectively, grain yield does not increase linearly with increasing N, but levels off at a threshold application rate (Figure 5). For spring barley, this would seem to lay between 90 to 120 kg N ha^{-1} (*14*). However, in terms of malting quality, the important criterion is that the protein content of the grain should be in the range of about 9 - 12%. This has still been achieved for the half-field rate fertilizer treatment (*14*). They concluded that reduce N fertilizer application rate may be acceptable strategy for low input arable agriculture. At low levels of soil N, competition between plant uptake and soil microbes favour plant assimilation such that proportionally less N_2O is produced than at higher fertilizer concentrations. In other words, if plants are better competitors for soil N than the pool of nitrifiers/denitrifiers, fluxes of N_2O will be relatively low (*14*, *56*). Nitrous oxide is also indirectly emitted from additions of N to soils and waters through conversion of N into gaseous ammonia (NH_3) and oxides of N, which are then returned to soil in the form of particulate ammonium (NH_4^+), nitric acid (HNO_3) and oxides of N. Surface run-off and leaching of applied N into ground water and surface waters can also result in indirect emissions of N_2O to the atmosphere (*88*).

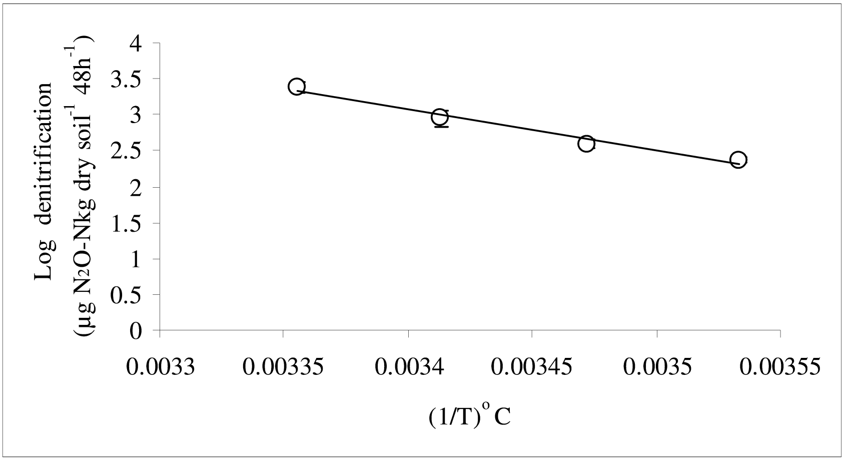


Figure 2. Arrhenius plot for calculation of activation energy showing correlation between cumulative denitrification and (1/T)° C. Each point represents the mean ± se of six measurements. $y = -5.724x + 22.533$, $r^2 = 0.98$. The relationship between incubation temperature and cumulative denitrification is represented by $y = 30.2e^{0.177x}$ ($r^2 = 0.98$). (Reproduced with permission from reference (20). Copyright 2009, British Society of Soil Science.)

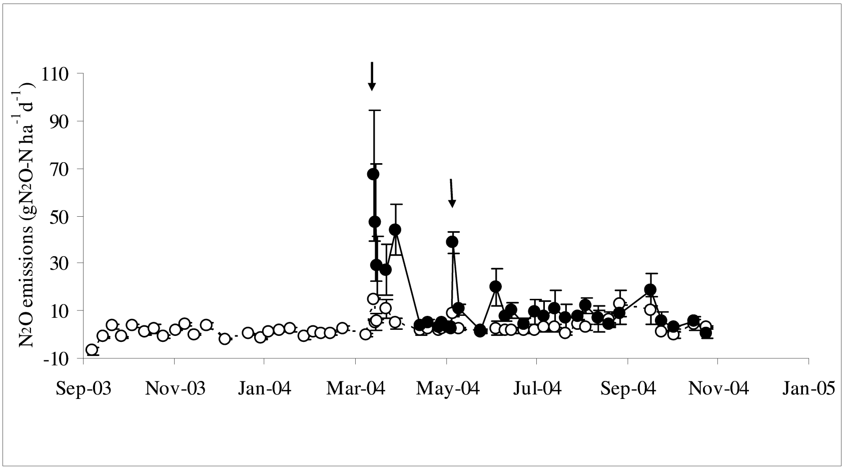


Figure 3. Daily N_2O emissions measured on a weekly basis from a cut and grazed pasture. Arrows indicate fertilizer application time (128kg N/ha, 72kg N/ha). Symbols indicate treatment at which N_2O flux was measured: fertilized plots (●) and control plots (○). Each point represents the mean ± se three to four replicates. (Reproduced with permission from reference (20). Copyright 2009, British Society of Soil Science.)

Mowing, Grazing, and Application of Manure

Mowing and grazing influence soil fertility indirectly by inducing changes in plant composition and demand for N by plants (*89*) and consequently increasing N_2O flux from soils. Mowing and grazing accelerate the N cycle (*90*) and encourage increased above- and below-ground plant growth (*91*) and root exudation (*92*). Plants in mown grasslands must complete their life cycle relatively early in the season, thus the recycling of roots from early-season species in mown fields boosts soil nutrient contents sooner than in un-mown fields (*93*). Mowing enables short-lived herbs that exploit early-season ecological niches (*94*), to flourish, and grazing reduces the dominance of grasses in favour of short-lived rosette species (*95*). Animal excreta deposited on pasture during grazing and application of manure or slurry by farmers represents major sources of N_2O emissions. Urine patches contain extremely high but localized concentrations of plant available N. These concentrations greatly exceed the uptake capacity of the grass, therefore, urine patches are especially susceptible to ammonia volatilization, denitrification and leaching (*96*). Higher N_2O emissions from animal excreta largely occur from cattle urine patches deposited under wet soil conditions in autumn and winter (*97*). Thus, the strategic use of a feed pad on dairy farms could restrict the amount of excreta N returned to pasture during this time of the year, and thus reduce N_2O emissions and other environmental losses (*98*).

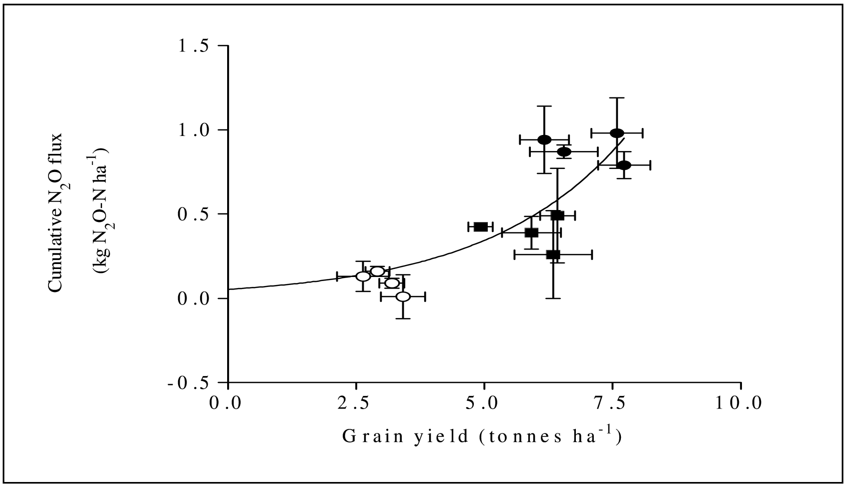


Figure 4. Relationship between grain yields of spring barley (at 15% moisture) and the cumulative flux of nitrous oxide flux over the growing seasons 2004/ 2005. Each point represents the mean ± se of 4 values. Symbols indicate fertilizer rate level: 140-159 (●), 70-79 (■) and zero kg N/ha (○). Line indicates curve of best fit where $y = 0.053*e^{0.373x}$, $(r^2 = 0.69)$. *(Reproduced with permission from reference (20). Copyright 2009, Springer Science + Business Media B.V.)*

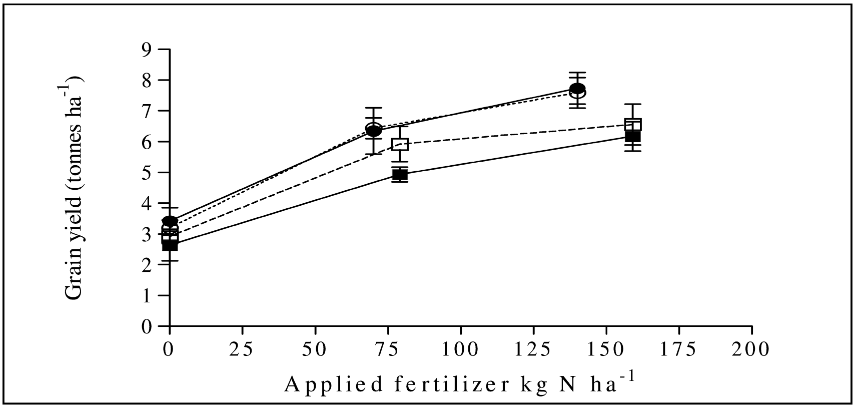


Figure 5. Relationship between N fertilizer application rate and grain yields from the conventional (CT) and reduced tillage (RT) for 2004 and 2005. Symbols indicate tillage/ year combination: CT 2004 (●), RT 2004 (○), CT 2005 (■) and RT 2005 (□). Each point represents the mean ± se of four measurements. (Reproduced with permission from reference (20). Copyright 2009, Springer Science + Business Media B.V.).

Nitrous oxide emissions from pasture and animal grazing are estimated as 28% of global anthropogenic N_2O emissions (*99*). High emissions of N_2O have been obtained from pig manure which contains a much higher total N than cattle manure (*100*). Moreover, dairy farming (*101*), burning of animal wastes (*102*) and application of animal manure (*103*) have large potentials for the production of N_2O. However, emissions of N_2O from organic crop rotation, in which only manure was used as N fertilizer, were significantly lower compared with N_2O emissions from conventional rotation where manure was mixed with N fertilizer (*104*).

Tillage Systems

Conventional seedbed preparation and sowing represents an inversion tillage which disturbs the soil to a depth of 20 to 25cm and may result in deterioration of soil structure and loss of soil organic matter from the system (*105*). Conventional tillage (CT) systems comprise of both primary and secondary cultivations. Primary tillage is the initial major operation that involves inverting the soil using a mouldboard plough (*106*). Secondary cultivation includes the use of a single or double pass of a cultivator to produce a seedbed for drilling using a cultivator drill (*107*). This system prepares a good seedbed by burying all surface residue and interrupting weed, pest and disease life cycles, giving the crop optimum germination conditions (*106*) because of the accelerated soil warming and drying that occurs prior to drilling (*108*). However, many researches have shown that ploughing can lead to soil-related problems (*109*) including soil compaction, soil erosion, emission of GHGs and lower work rates. The intensive tillage under the plough leaves the soil bare and exposed to rainfall and high wind speeds accelerating erosion and degrading processes that reduce agronomic productivity and soil quality (*110*).

An alternative to this is non-inversion-tillage (NIT), also known as reduced tillage, no-tillage, ECO-tillage, minimum tillage or conservation tillage is a form of tillage management disturbs the surface soil to a depth of 10-15cm (*111*). Worldwide, NIT is practiced on 45 M ha, predominantly in North and South America (*112*), whilst only approximately 10 million ha have been under NIT cultivation in Europe (*113*).

NIT can include various types of cultivation equipment that disturb the surface of the soil without inversion, and incorporate to varying degrees the stubble of the previous crop. The percentage of crop residue left on the soil surface has been used as a way of defining NIT, i.e. over 30 % cover of previous crop residue (*114*). Weed control is accomplished with the use of herbicides and cultivation. Non-inversion tillage systems require less energy than conventional systems, and facilitate faster land preparation allowing a large area to be sown within the optimum time frame for successful crop establishment (*115*). NIT reduces soil erosion, has low labour intensity and hence lowers costs (*116*). In addition in dry and humid climates at least, NIT has been found to be effective in mitigating GHG emissions (*117*). However, this may not always be the case. Some studies have shown NIT to produce initially larger (*118*, *119*) or similar (*120*, *121*) fluxes of N_2O as conventional tillage. In study on spring barley field, (*14*) found reduced tillage had no significant effects on N_2O fluxes compared with the conventional tillage however, there was a trend of slightly higher N_2O flux from reduced tillage (Table I). Adopting of reduced tillage in the short run, as a means for mitigating N_2O fluxes from the soil would not be successful. Initial increases in N_2O flux from non inversion tillage have been a consistent observation in the literature (*118*, *122*, *123*). These increases may need a period of at least 10 years to return to background levels and 20 years to see any mitigation effects on greenhouse gas emissions in general (*124*). A long-term N simulation study by (*119*), found that NIT could increase N_2O fluxes from a maize/ soybean rotation in Iowa, USA offsetting 75% of carbon sequestered due to increasing soil organic carbon.

Cover Crop

A cover crop is any crop grown to provide soil cover, regardless of whether it is later incorporated. A cover crop is grown primarily to prevent soil erosion by wind and water and to retain nutrients in organic farming. It can be annual, biennial, or perennial herbaceous plants grown in a pure or mixed stand during all or part of the year. Legume cover crops may reduce N fertilizer requirements by fixing N biologically and storing left over N-fertilizer applied in the previous year, whereas non legumes are excellent at absorbing excess nutrients in the soil, increasing plant biomass, and improving soil tilt (*125*). In addition cover crop is an effective strategy in reducing the soil nitrate pool and therefore, N_2O fluxes from soils (*125*). Cover crop reduced the nitrate concentration in leachate by 20 to 80% (*126*). Moreover, rye cover crop accumulated a significant proportion of manure-N, greatly reduced the amount of NO_3 lost in drainage water, reduced soil inorganic N levels, increased evapo-transpiration, reduced cumulative drainage and reduced N_2O emissions (*127*).

Crop Residue

Application of crop residues to soil has been shown to increase N_2O emissions (*128*). Crop residues activate aerobic decomposition following that, the drawdown of oxygen activates denitrification (*128*). Applying crop residues to the soil and mineralizing it generally increases N_2O production because organic C is used in the mineralization processes. Nitrogen in crop residues is in organic form and is not directly available for plant growth. However, during decomposition of crop residues, this organically bound N is made available for crop or microbial growth through N mineralization (*129*).

Major factors affecting the impact of crop residues on nutrient availability include residue quality, soil characteristics and environmental conditions (*130*). Applying crop residues with a low C:N ratio encourages mineralization (*131*) and N_2O emissions (*132*), but applying residues with a higher C:N ratio advances N immobilization. In one study (*133*), negative logarithmic relationship between N_2O emission and the C:N ratio of applied organic matter at the same N application rate in an Andisol field was reported. Whereas in another study (*134*), the ratio of N_2O emission to applied residue N increased with increasing C:N ratio of residues.

Leguminous Crops

Legumes can have both direct and indirect effect on N_2O emissions. The indirect effect is by increasing the amount of N cycling through the plant-soil system, which can be nitrified or denitrified to N_2O in the same way as fertilizer N. Emissions of N_2O from biologically fixed N is probably less than from fertilizer N (*135*). Legumes can increase N_2O emissions by a factor of 2 or 3 (*136*). Globally, estimated N_2O emissions from fields of cultivated leguminous crops are in the range of 23 to 315 Gg N_2O-N y^{-1} (*137*). Legume crops could have a direct effect on N_2O emission if they provide significant rhizobial denitrification (*138*). A previous study considered N_2O emission directly from rhizobial denitrification to be slightly greater than the background emission from agricultural crops (*139*). However, the IPCC's methodology 2006 assumes that emissions from N fixation are zero (*140*).

Simulating of N_2O Emissions and Response to Climate Change

Increases in surface air temperature due to climate change would be expected to increase evaporation leading to higher levels of atmospheric water vapor and a greater variability in the frequency and extent of rainfall (*141*, *142*). The relationship between temperature and higher N_2O flux has been reported by many researchers (e.g. (*55*, *64*, *143–147*)). Higher rainfall due to climate change also positively influenced N_2O fluxes from soils (*36*, *148*, *149*). Temperature and precipitation are the major factors affecting N mineralization and denitrification and consequently N_2O fluxes from soils (*150–153*).

Table I. Grain yields, cumulative N_2O-N emitted and emission factors for the conventional and reduced tillage plots in 2004/2005. Each value represents the mean ± se of four replicate values. (Reproduced with permission from reference (*20*). Copyright 2009, Springer Science + Business Media B.V.)

Treatment	*Grain yields (t/ha), cumulative N_2O emissions (kg N_2O-N/ha) and EF (%)*					
2004	*Conventional tillage*			*Reduced tillage*		
140 kg N ha^{-1}	7.73	0.79 ± 0.08	0.63 ± 0.06	7.58	0.98 ± 0.21	0.63± 0.20
70 kg N ha^{-1}	6.34	0.26 ± 0.26	0.42 ± 0.41	6.43	0.49 ± 0.28	0.65 ± 0.45
0 kg N ha^{-1}	3.41	0.01 ± 0.13	-	3.20	0.09 ± 0.03	-
2005						
159 kg N ha^{-1}	6.55	0.87 ± 0.04	0.61 ± 0.03	6.17	0.94 ± 0.2	0.65 ± 0.41
79 kg N ha^{-1}	5.92	0.39 ± 0.10	0.54 ± 0.13	4.93	0.42 ± 0.02	0.59 ± 0.03
0 kg N ha^{-1}	2.91	0.16 ± 0.03	-	2.64	0.13 ± 0.09	-

Nitrous oxide emission is important for global warming therefore, regional or even global emission estimates are needed for policy and decision makers. Given the considerable expense of establishing and maintaining relevant flux measurement sites, the use of simulation models to estimate N_2O fluxes from agricultural soils, using soil and climate data, has obvious benefits. Modelling also allows the complex links between soil physical, chemical and microbial processes that underpin nitrification, denitrification and decomposition to be examined. Models can simulate the processes responsible for production, consumption and transport of N_2O in both the short and long term, and also allow spatial simulation (*154*). Simulation models range from simple empirical relationships based on statistical analyses to complex mechanistic models that consider all factors affecting N_2O production in the soil (*155*). DayCent (Daily Century) and DNDC (DeNitrification-DeComposition) models are two widely-used ecosystem biogeochemistry models used to estimate N_2O emissions. DayCent model is the daily time-step version of the CENTURY biogeochemical model (*156*).

Comparison of model outputs and observed data have shown that DayCent reliably simulates crop yield, soil organic matters (SOM) levels, and trace-gas flux for various native and managed systems (*157*, *158*). DNDC model was developed to assess N_2O, NO, N_2 and CO_2 emissions from agricultural soils (*155*). This rainfall driven process-based model was originally developed for USA conditions (*155*). However, it has been used for GHG simulation at a regional scale for the USA (*159*), China (*160*), Canada (*161*) and Europe (*162*). DNDC is suitable for simulation of C and N dynamics from arable soil in medium to high N input systems (70 to 160 kg N ha^{-1}), but less suitable for low N input systems (control), with the accuracy of the prediction being highly dependant on the level of N fertilizer application rate (*163*). High fertilizer inputs produce low relative deviations (~1-6%) between modelled and observed fluxes for the arable field under conventional tillage (*163*). However, prediction of N_2O fluxes from reduced tillage was poor with DNDC consistently underestimating observed values (-20 to -93%). One major disadvantage of the model was the limited choice of tillage input options available, none describing all NIT treatment types (e.g at 15cm depth). Overall DNDC model underestimated the seasonal flux from arable field by 24% (Figure 6; (*163*)).

Prediction of N_2O fluxes from grassland using DNDC was poor with the model outputs significantly overestimating observed values (150 to 360%). DNDC simulated significantly higher N_2O peaks, from both the control and fertilized grasslands. The model is very sensitive to higher SOC and WFPS in the grassland and therefore, overestimating nitrification and denitrification (*163*). However, DayCent model effectively estimates N_2O fluxes and biomass production from fertilized grassland with relative deviations from the observed values of +38% (RMSE = 2) and (-23%) (RMSE = 0.15), respectively (*164*). Under unfertilized grassland DayCent underestimated the observed N_2O flux by 57% (RMSE = 0.5).

Climate feedback could have significant impacts on N_2O fluxes from soils. Soil nitrogen increases due to increasing mineralisation with changing temperature and precipitation (*151*). However, the climate impact on nitrous oxide emissions from arable soil largely depended on the tillage types. For conventional tillage, three peaks of N_2O emissions were predicted; an early spring peak coinciding mostly with soil ploughing, a mid/ late spring peak coinciding with fertilizer application and an early autumn peak coinciding with residue incorporation and onset of autumn rainfall (Figure 7). For reduced tillage, due to the less amount of soil disturbance, the early spring peak was not predicted (Figure 7). In all cases the total amount of N_2O emitted in the late spring peak due to fertilizer application was less than the sum of the other peaks (*151*). DNDC predicted an increase in N_2O emissions from both conventional and reduced tillage, ranging from 58 to 88% depending upon N application rate (Table II). Outputs from the model indicate that elevated temperature and precipitation increase N mineralisation and total denitrification leading to greater fluxes of N_2O (Tables III and IV). With increasing temperature, nitrous oxide fluxes from both tillage systems would significantly increase compared with the baseline climate. Although, reduced tillage is known with its ability to sequester C in the soil, DNDC predicted significant increase in N_2O flux, compared with conventional tillage, with climate change due to increasing temperature. Nitrous oxide flux patterns and peak heights depend on the tillage type. The differences in cumulative flux between the two tillage treatments increase with climate change.

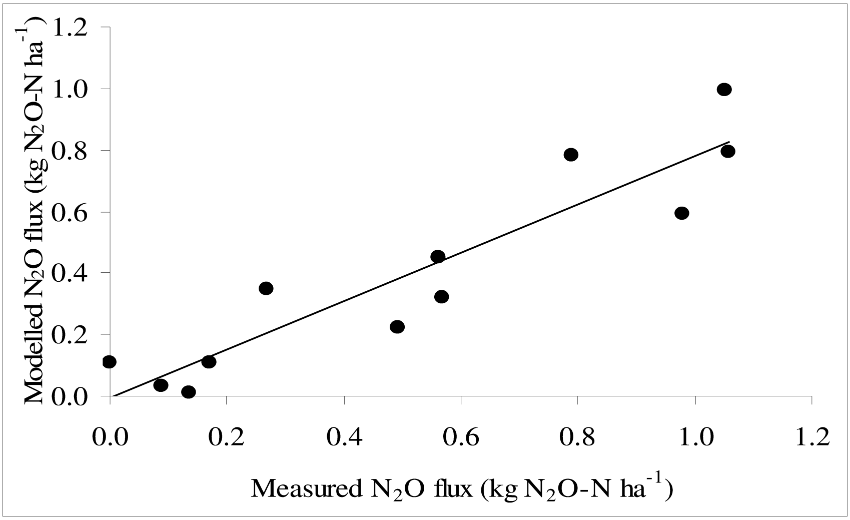


Figure 6. Correlation between the field measured and model-simulated N_2O fluxes for the arable field. $y = 0.78x - 6.5$ ($r^2 = 0.85$). (Reproduced with permission from reference (163). Copyright 2009, Elsevier.)

DayCent predicted no significant effect on N_2O flux from sandy loam soils, due to climate change (Figure 8; (*164*)). This is due to the considerably greater demand for N from enhanced grass growth under climate change (Figure 9). The amount of available soil N, in excess of the N requirement of the grass decreased, resulting in low N_2O flux. Nitrous oxide has a threshold response to N, and the amount of N lost to atmosphere depends on the amount of N taken by the crop (*14*, *56*). Soil mineral nitrogen and N mineralization are the main sources of N_2O production (*164*, *165*). Therefore, future N_2O flux from this grassland field may not be significantly affected by climate change, unless more N fertilizer is applied. The future higher above ground biomass production predicted by DayCent would encourage farmers to increase grazing intensity. This would increase emissions of methane (CH_4) and excretal N deposition from grazing animals. Alternatively, farmers could apply less N fertilizer to the pasture to achieve the current amount of above ground biomass production without making significant change on N_2O or CH_4 fluxes (*164*).

Table II. Simulated cumulative N_2O emissions (kg N_2O-N ha^{-1}) under different N fertilizer levels, tillage systems and climate scenarios: baseline, high temperature sensitive (HTS) and low temperature sensitive (LTS). Values with different letters, within each year, are significantly different from each other (P<0.05). (Reproduced with permission from reference (*151*). Copyright 2009, Springer-Verlag.)

Treatment	*Cumulative N_2O emissions (kg N_2O-N ha^{-1}) and future change (%) compared with the baseline*					
N applied once (year 2004)	*Conventional tillage*			*Reduced tillage*		
	base-line	*HTS*	*LTS*	*base-line*	*HTS*	*LTS*
140 kg N ha^{-1}	5.5 a	9.8 ab	5.7 a	5.9 a	11 ab	6.5 a
70 kg N ha^{-1}	4.9 b	8.6 ac	4.5 b	5.5 b	9.9 ac	5.3 b
0 kg N ha^{-1}	4.0 c	6.9 bc	3.1 c	5.0 c	9.0 abc	4.4 c
N split into two (year 2005)						
159 kg N ha^{-1}	5.7 a	10.6 ab	6.4 a	6.3 a	11.8 ab	7.3 a
79 kg N ha^{-1}	5.0 b	8.9 ac	4.8 b	5.7 b	10.2 ac	5.6 b
0 kg N ha^{-1}	4.2 c	6.6 bc	3.1 c	5.0 c	8.9 abc	4.4 c

Table III. Simulated mineralization (kg N ha^{-1}) under different N fertilizer levels, tillage systems and climate scenarios: baseline, high temperature sensitive (HTS) and low temperature sensitive (LTS). Values with different letters, within each year, are significantly different from each other (P<0.05). (Reproduced with permission from reference (*151*). Copyright 2009, Springer-Verlag.)

Treatment	*N mineralization (kg N ha^{-1}) and future change (%) compared with the baseline*					
N applied once (year 2004)	*Conventional tillage*			*Reduced tillage*		
	base-line	*HTS*	*LTS*	*base-line*	*HTS*	*LTS*
140 kg N ha^{-1}	329.5 a	416.1 ab	362.2 a	339.9 a	429.7 ab	376.8 a
70 kg N ha^{-1}	323.9 b	401.1 ac	346.2 b	334.9 b	413.7 ac	359.4 b
0 kg N ha^{-1}	298.5 c	367.7 bc	310.8 c	308.2 c	377.1 abc	321.6 c
N split into two (year 2005)						

Continued on next page.

Table III. (Continued). Simulated mineralization (kg N ha^{-1}) under different N fertilizer levels, tillage systems and climate scenarios: baseline, high temperature sensitive (HTS) and low temperature sensitive (LTS). Values with different letters, within each year, are significantly different from each other (P<0.05).

Treatment	*N mineralization (kg N ha^{-1}) and future change (%) compared with the baseline*					
N applied once (year 2004)	*Conventional tillage*			*Reduced tillage*		
	base-line	*HTS*	*LTS*	*base-line*	*HTS*	*LTS*
159 kg N ha^{-1}	328.0 a	416.0 ab	362.2 bc	342.5 a	429.5 ab	376.9 a
79 kg N ha^{-1}	323.9 b	401.2 ac	346.3 b	335.0 b	413.7 ac	359.5 b
0 kg N ha^{-1}	333.7 c	421.8 bc	365.2 cc	308.2 bb	377.1 abc	321.6 c

Table IV. Simulated annual denitrification (kg N ha^{-1}) under different N fertilizer levels, tillage systems and climate scenarios: baseline, high temperature sensitive (HTS) and low temperature sensitive (LTS). Values with different letters, within each year, are significantly different from each other (P<0.05). (Reproduced with permission from reference (*151*). Copyright 2009, Springer-Verlag.)

Treatment	*Denitrification (kg N ha^{-1}) and future change (%) compared with the baseline*					
N applied once (year 2004)	*Conventional tillage*			*Reduced tillage*		
	base-line	*HTS*	*LTS*	*base-line*	*HTS*	*LTS*
140 kg N ha^{-1}	14.7 a	27.1 ab	14.4 a	15.4 a	26.3 ab	15.5 a
70 kg N ha^{-1}	12.6 b	24.6 ac	12.3 b	13.4 b	23.6 ac	12.7 b
0 kg N ha^{-1}	9.3 c	19.3 bc	9.2 c	11.2 c	21.8 bc	10.7 c
N split into two (year 2005)						
159 kg N ha^{-1}	15.7 a	29.1 ab	15.7 a	16.5 a	29.0 ab	17.0 a
79 kg N ha^{-1}	13.1 b	25.6 ac	13.0 b	14.1 b	25.1 ac	13.7 b
0 kg N ha^{-1}	10.2 c	15.2 bc	10.7 c	11.2 c	21.8 abc	10.7 c

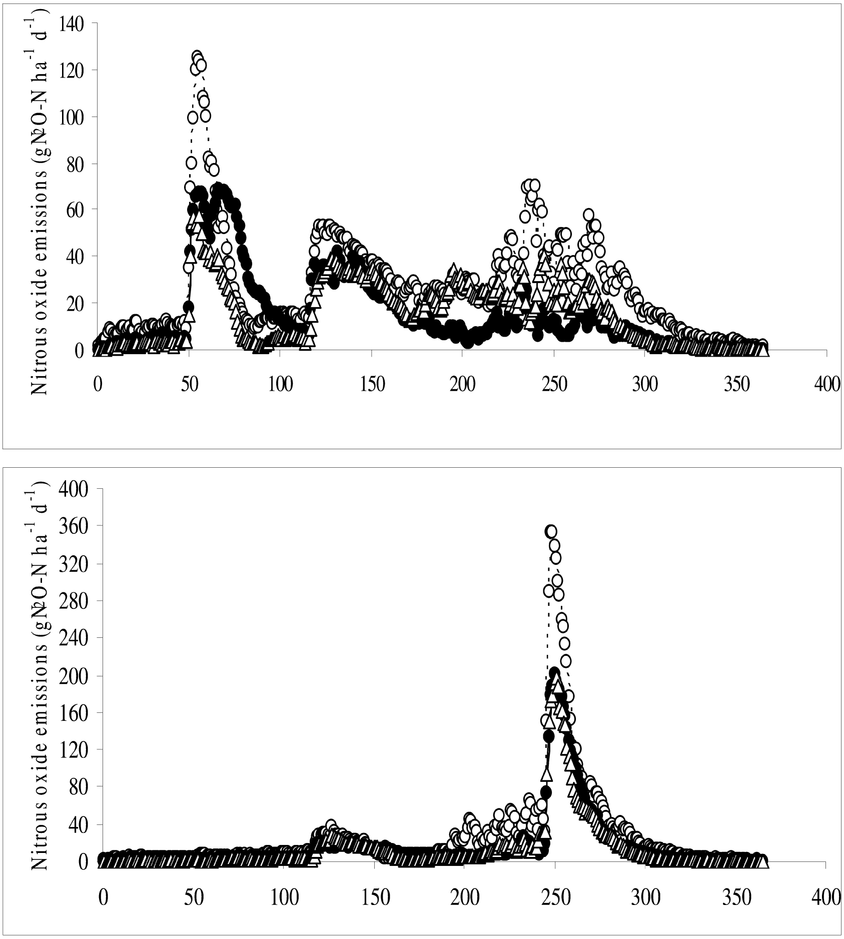


Figure 7. Effects of climate change on N_2O emissions for conventional (upper) and reduced (lower) tillage under 140 kg N fertilizer application for the high (○) and low (Δ) temperature sensitive climate data compared with measured baseline climate (●). (Reproduced with permission from reference (151). Copyright 2009, Springer-Verlag.)

Possible Mitigation Options

Nitrous oxide release from nitrification and denitrification are closely linked to other N transformations and loss processes, such as nitrate leaching and ammonia volatilisation (*96*). As a result, management options to reduce one loss process could potentially enhance other environmental problems (*166*). Moreover, options that may reduce direct emissions of N_2O, but potentially increase nitrate leaching or ammonia volatilisation, could also enhance the indirect emissions of N_2O. Therefore, mitigation option for reducing N_2O emissions should consider the nitrogen cycle of agricultural systems as whole, and aim to increase the N efficiency of these systems.

Several options are available for reducing N_2O emissions from agriculture. Direct soil emissions can be mitigated by reducing N input to the soils, e.g. by a more efficient use of N in agriculture (*14*, *167*). Application of nitrogen fertilizer enhances yield, accelerating the nitrogen cycle (*168*); thus better N use efficiency and minimized N_2O emission per unit of crop yield is a good option (*169*). Replacing synthetic fertilizer by manure can reduce N_2O emissions, but efficient use of manure is required (*167*). Low nitrogen feed assumes changes in the composition of feed such that the N content decreases. This reduces N excreted emissions of N_2O (*170*). Restrictions on the timing of fertilizer application will reduce N_2O from soil as well as from nitrogen leaching and maximize N uptake by plants (*171*). Restricting grazing in dairy farming systems reduced autumn N_2O emissions by 7 - 11% (*98*). Fertilizer type is also an option for mitigation of N_2O emissions, especially the use of slow-release fertilizers to controlled supply of substrate provided for denitrifiers (*172*).

The use of advanced fertilisation techniques like using a nitrification inhibitor, placing fertilizer below ground, using foliar feed fertilizers or matching fertilizer type to seasonal conditions, can play a great role in reducing N_2O emissions (*167*). For example, (*173*) noted that the addition of nitrification inhibitor dicyandiamide (DCD) to calcium ammonium nitrate fertilizer or slurry reduced cumulative N_2O losses by about 42 and 60% respectively. Application of DCD after application of urine reduced N_2O emissions by up to 78% (*174*).

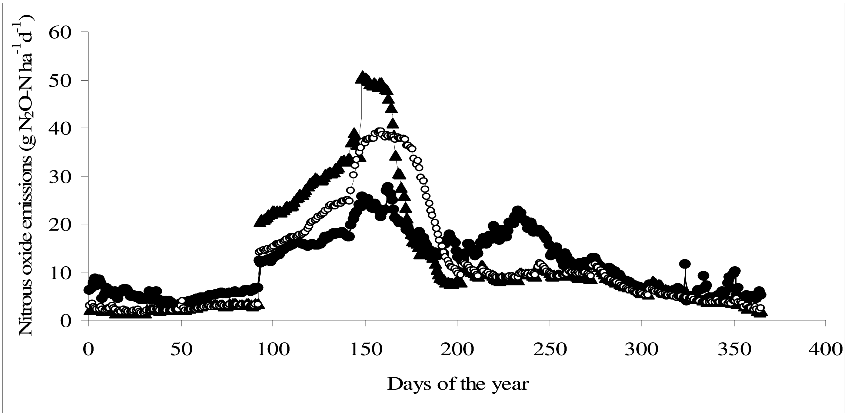


Figure 8. Effects of climate change on N_2O emissions from the grass field for the high (▲) and low (○) temperature sensitive climate data compared with measured baseline climate (●). (Reproduced with permission from reference (164). Copyright 2010, Elsevier.)

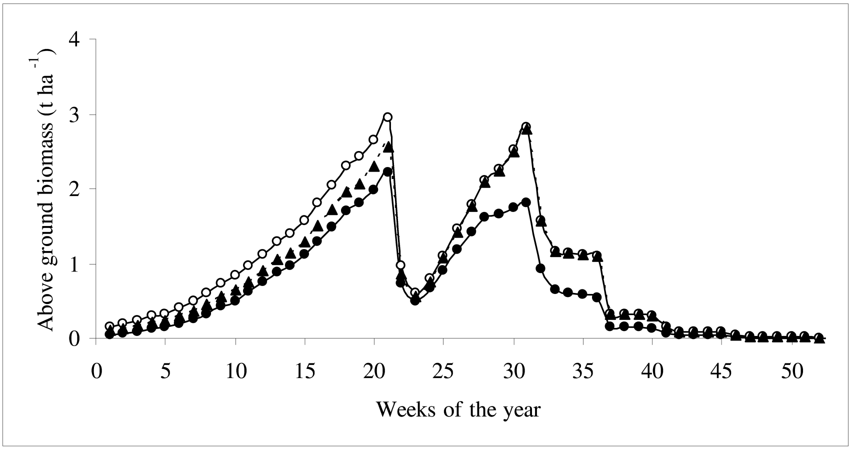


Figure 9. Effects of climate change on above ground grass biomass production for the high (○) and low (▲) temperature sensitive climate scenarios compared with measured baseline climate (●). (Reproduced with permission from reference (164). Copyright 2010, Elsevier.)

An alternative approach to mitigating N_2O emissions is to manipulate the end product of denitrification. The two main end products of denitrification are N_2O and N_2 (*167*). Therefore, enhancing the conversion of N_2O to N_2 can reduce N_2O emissions. However, the ratio at which N_2O and N are produced during denitrification is very variable and depends on numerous soil and environmental factors. This hampers the development of mitigation options to reduce N_2O/ N_2 ratio. Strong relative relationship between soil pH and the N_2O/ N_2 ratio was found and suggested that maintaining the soil pH at about 6.5 might help maintain a low mole fraction from denitrification (*175*, *176*).

Conclusions

1. Agriculture is the main source of nitrous oxide emissions to the atmosphere. For grassland soils, >60% of the annual fluxes are associated with fertilizer application time however, for the arable soils the total fluxes during the crop post harvested period are exceeding the fluxes due to N fertilizer.

2. Adopting of reduced tillage in the short run, as a means for mitigating N_2O fluxes from the soil wouldn't be successful. To see any mitigation effects on greenhouse gas emissions in general this may need 20 years.

3. Reducing fertilizer application rate by 50% is an acceptable strategy for low input agriculture in that there was no significant effect on grain yield or quality in terms of required protein content, but seasonal emissions of N_2O were significantly reduced. Nitrous oxide flux has a threshold response to N fertilization where the amount of N lost to the atmosphere depends on the amount of N taken up by the crop.

4. Mowing and grazing influence soil fertility indirectly by induce changes in plant composition and consequently increase N_2O flux from soils.

5. Application of cover crop is an effective strategy in reducing the soil nitrate pool and therefore, N_2O fluxes whilst application of leguminous crops may reduce N fertilizer requirements by fixing N biologically and storing left over N-fertilizer applied in the previous year.

6. Given the considerable expense of establishing and maintaining relevant flux measurement sites, the use of simulation models like DNDC and DayCent to estimate N_2O fluxes from agricultural soils using soil and climate data has obvious benefits.

7. Future warming temperature will significantly increase N_2O flux from arable soils due to higher mineralization and denitrification however, the increase depends on the tillage type. Here, N_2O flux from reduced tillage would significantly increase compared with conventional tillage.

8. Climate change is not expected to significantly affect N_2O fluxes from low N input grassland. This is due to the significant grass growth and higher N demand by the grass under climate change.

Acknowledgments

This work was funded by the EU sixth framework program (contract EVK2-CT2001-00105) and Irish EPA. We are grateful to Mike Jones, Per Ambus, Martin Wattenbach, James Burke and Jagadeesh Yeluripati. We are also grateful to the Irish National Meteorological Service Research Group (Met Éireann) for providing us with the Community Climate Change Consortium for Ireland (C4I) projections data.

References

1. Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; Van Dorland, R. In *Climate Change 2007: The Physical Science Basis*; Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge Univ. Press: Cambridge, NY, 2007; pp 129−234.
2. Crutzen, P. J. *Q. J. R. Meteorol. Soc.* **1976**, *96*, 320–325.
3. Ravishankara, A. R.; Daniel, J. S.; Portmann, R. W. *Science* **2009**, *326*, 123–125.
4. Houghton, J. T., Meira Filho, L. G., Callander, B. A., Harris, N., Kattenberg, A., Maskell, K., Eds.; *Climate Change 1995: The Science of Climate Change*; Cambridge University Press" Cambridge, U.K, 1996; p 572.
5. IPCC, 2007. In *Climate Change 2007: The Physical Science Basis*; Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor M., Miller, H. L., Eds.; : Cambridge, United Kingdom, 2007; pp 1−18.
6. IPCC. *Climate change 2001, Third assessment Report of the IPCC*; Cambridge University Press: U.K.

7. WHO, 2000. World Health Organization, European Series No. 91. Geneva, Switzerland, p 273.
8. Frankhauser, S.; Tol, R. *Energy Policy* **1996**, *24*, 665–673.
9. Kroeze, C.; Mosier, A.; Bouwman, L. *Global Biogeochem. Cycles* **1999**, *12*, 1–8.
10. IPCC, 1996. *Climate change, the Science of Climate Change 1995*; Cambridge University Press: Cambridge, U.K.
11. Wrage, N.; Velthof, G. L.; Laanbroek, H. J.; Oenema, O. *Soil Biol. Biochem.* **2004**, *36*, 229–236.
12. Robertson, G. P. In *The Global Carbon Cycle*; Field, C. B., Raupach, M. R., Eds.; Island Press: Washington, DC , 2004; pp 493–506..
13. Hutchinson, G. L; Davidson, E. A. In *Agricultural Ecosystem Effects on trace gases and global Climate Change*; Harper, L. A., Mosier, A. R., Duxbury, J. M., Rolston, D. E., Eds.; ASA Special Publication No. 55. A Soci Agron: Madison, WI, 1993; pp. 79-94.
14. Abdalla, M.; Jones, M.; Ambus, P.; Williams, M. *Nutr. Cycling Agroecosyst.* **2010**, *86*, 53–65.
15. Freibauer, A.; Kaltschmitt, M. *European summary report of the EU concerted action 'Biogenic emissions of Greenhouse Gases caused by arable and animal agriculture'*; 2000. (FAIR3-CT96-1877).
16. Hack-ten Broeke, M. J. D.; Schut, A. G. T.; Bouma, J. *Geoderma* **1999**, *91*, 217–235.
17. Denmead, O. T.; Leuning, R.; Jamie, I.; Griffith, D. W. T. *Chemosphere: Global Change Sci.* **2000**, *2*, 301–312.
18. IPCC. *Revised 1996 IPCC guidelines for national greenhouse gas inventories*; IPCC/OECD/IEA, IPCC: Geneva, Switzerland, 1997.
19. Bremner, J. M.; Blackmer, A. M. *Science* **1978**, *199*, 295–296.
20. Abdalla, M.; Jones, M.; Smith, P.; Williams, M. *Soil Use and Manag* **2009**, *25*, 376–388.
21. Wrage, N.; Velthof, G. L.; Van Beusichem, M. L.; Oenema, O. *Soil Biol. Biochem.* **2001**, *33*, 1723–1732.
22. Stevens, R. J.; Laughlin, R. J.; Burns, L. C.; Arah, J. R. M.; Hood, R. C. *Soil Biol. Biochem.* **1997**, *29*, 139–151.
23. Troeh, F. R.; Thompson, L. M. *Soils and soil fertility*, 6th ed.; Blackwell Publishing, 2005.
24. Robertson, G. P.; Vitousek, P. M. *Ecology* **1981**, *62*, 376–386.
25. Robertson, G. P.; Tiedje, J. M. *Soil Sci. Soci. Am. J.* **1984**, *48*, 383–389.
26. Christensen, N. L.; MacAller, T. *Soil Biol. Biochem.* **1985**, *17*, 675–681.
27. Bramley, R. G. V.; White, R. E. *Plant Soil* **1990**, *126*, 203–208.
28. Patureau, D.; Zumstein, E.; Delgenes, J. P.; Moletta, R. *Microb. Ecol.* **2000**, *39*, 145–152.
29. Carter, J. P.; Hsaio, Y. H.; Spiro, S.; Richardson, D. J. *Appl. Environ. Microbiol.* **1995**, *61*, 2852–2858.
30. Meyer, J. L. *Microb. Ecol.* **1994**, *28*, 195–199.
31. Duggin, J. A.; Voigt, G. K.; Bormann, F. H. *Soil Biol. Biochem.* **1991**, *23*, 779–787.

32. Downs, M. R.; Nadelhoffer, K. J.; Mellilo, J. M.; Aber, J. D. *Oecologia* **1996**, *105*, 141–150.
33. Tiedje, J. M. In *Methods of soil analysis, part 2*, 2nd ed.; Page, A. L., Miller, R. H., Keeney, D. R., Ed.; Soil Science Society of America, Inc.: Madison, WI, 1982; Vol. 9, pp 1011−1026.
34. Simek, M.; Jisova, L.; Hopkins, D. W. *Soil Biol. Biochem.* **2002**, *34*, 1227–1234.
35. Bowden, W. B.; Bormann, F, H. *Science* **1986**, *233*, 867–869.
36. Dobbie, K. E.; McTaggart, I. P.; Smith, K. A. *Geophys. Res. Lett.* **1999**, *104*, 26891–26899.
37. Abassi, M. K.; Adams, W. A. *Soil Biol. Biochem.* **2000**, *32*, 1251–1259.
38. Skiba, U.; Ball, B. *Soil Use Manag.* **2002**, *18*, 56–60.
39. Tiedje, J. M. In *Biology of anaerobic micro organism*; Zehnder, A. J. B., Ed.; Wiley and Sons: New York, 1988; pp 179−244.
40. Burford, J.; Bremner, J. M. *Soil Biol. Biochem.* **1975**, *11*, 261–267.
41. Wagner-Riddle, C.; Thurtell, G. W.; King, K. M.; Kidd, G. E.; Beauchamp, E. G. *Environ. Qual.* **1996**, *25*, 898–907.
42. Schlesinger, W. H.; Peterjohn, W. T. *Soil Biol. Biochem.* **1991**, *23*, 637–642.
43. šimek, M.; Cooper, J. E. *Eur. J. Soil Sci.* **2002**, *53*, 345–354.
44. Barrios, E.; Buresh, R. J.; Sprent, J. I. *Soil Biol. Biochem.* **1996**, *282*, 185–193.
45. Khalil, M. I.; Rosenami, A. B.; Cleemput, O. V.; Boeckx, P.; Shamshuddin, J.; Fauziah, C. I. *Biol. Fertil. Soils* **2002**, *36*, 59–65.
46. Ball, B. C.; Horgan, G. W.; Clayton, H.; Parker, J. P. *Environ. Qual.* **1997**, *26*, 1399–1409.
47. Castaldi, S.; Smith, K. A. *Plant Soil* **1998**, *199*, 229–238.
48. McKenzie, A. F.; Fan, M. X.; Cardin, F. *Environ. Qual.* **1998**, *27*, 698–703.
49. Kaiser, E. A.; Kohrs, K.; Kucke, M.; Schnug, E.; Heinemeyer, O.; Munch, J. C. *Soil Biol. Biochem.* **1998**, *30*, 1553–1563.
50. Mahmood, T.; Ali, R.; Malik, K. A.; Shamsi, S. R. A. *Biol. Fertil. Soils* **1998**, *27*, 189–196.
51. Blackmer, A. M.; Robbins, S. G.; Bremner, J. M. *Soil Sci. Soc. Am. J.* **1982**, *46*, 937–942.
52. Choudhary, M. A.; Akramkhanov, A.; Saggar, S. *Agric. Ecosyst. Environ.* **2002**, *93*, 33–43.
53. Dobbie, K. E; Smith, K. A. *Global Change Biol.* **2003**, *9*, 204–218.
54. Rudaz, A. O.; Walti, E.; Kyburz, G.; Lehmann, P.; Fuhrer, J. *Agric., Ecosyst. Environ.* **1999**, *73*, 83–91.
55. Wang, Y.; Xue, M.; Zheng, X.; Ji, B.; Du, R.; Wang, Y. *Chemosphere* **2005**, *58*, 205–215.
56. McSwiney, C. P; Robertson, G. P. *Global Change Biol.* **2005**, *11*, 1712–1719.
57. Maljanen, M.; Martikainen, P. J.; Aaltonen, H. *Soil Biol. Biochem.* **2002**, *34*, 577–584.
58. Dobbie, K. E; Smith, K. A. *Eur. J. Soil Sci.* **2001**, *52*, 667–673.
59. Keller, M.; Reiners, W. A. *Global Biogeochem. Cycles* **1994**, *8*, 399–409.
60. Veldkamp, E.; Keller, M.; Nunez, M. *Global Biogeochem. Cycles* **1998**, *12*, 71–79.

61. Ruser, R.; Flessa, H.; Schilling, R.; Steidl, H.; Beese, F. *Soil Sci. Soc. Am. J.* **1998**, *62*, 1587–1595.
62. Addiscott, T. M. *Soil Sci.* **1984**, *34*, 343–353.
63. Scott, D. E.; Elliott, L. F.; Papendick, R. I.; Campbell, G. S. *Soil Biol. Biochem.* **1986**, *18*, 577–582.
64. Flessa, H.; Ruser, R. *Geoderma* **2002**, *105*, 307–325.
65. Skiba, U.; Hargreaves, K. J.; Beverland, I. J.; O' Neill, D. H.; Fowler, D.; Moncrieff, J. B. *Plant Soil* **1996**, *181*, 139–144.
66. Christensen, S. *Soil Biol. Biochem.* **1983**, *15*, 531–536.
67. Matson, P. A; Vitousek, P. M.; Livigston, G. P.; Swanberg, N. A. *Geophy. Res.* **1990**, *95*, 16789–16798.
68. Sanhueza, E.; Hao, W. M.; Scharffe, D.; Donoso, L.; Crutzen, P. J. *Geophy. Res.* **1990**, *95*, 22481–22488.
69. McKeeney, D. R.; Fillery, I. R.; Marx, J. P. *Soil Sci. Soc. Am. J.* **1979**, *43*, 1124–1128.
70. Van Bochove, E.; Jones, H. G.; Pelletier, F.; Prevost, D. *Hydrol. Processes* **1996**, *10*, 1545–1549.
71. Wanger-Riddle, C.; Thurtell, G. W.; Kidd, G. K.; Beauchamp, E. G.; Sweetman, R. *Can. J. Soil Sci.* **1997**, *77*, 135–144.
72. Alm, J.; Saarnio, S.; Nyka¨ nen, H.; Silvola, J.; Martikainen, P. J. *Biogeochemistry* **1999**, *44*, 163–189.
73. Teepe, R.; Brumme, R.; Beese, F. *Soil Biol. Biochem.* **2000**, *32*, 1807–1810.
74. Koponen, H. T.; Flo¨jt, L.; Martikainen, P. J. *Soil. Biol. Biochem.* **2004**, *36*, 757–766.
75. Oquist, M. G.; Nilsson, M.; Sorensson, F.; Kasimir-Klemedtsson, A.; Persson, T.; Weslien, P.; Klemedtsson, L. *FEMS Microbiol. Ecol.* **2004**, *49*, 371–378.
76. Teepe, R.; Brumme, R.; Beese, F. *Soil Biol. Biochem.* **2001**, *33*, 1269–1275.
77. Premie, A.; Christensen, S. *Soil Biol. Biochem.* **2001**, *33*, 2083–2091.
78. Bruton, D. L.; Beauchamp, E. G. *Soil Sci. Soc. Am. J.* **1994**, *58*, 115–122.
79. Christensen, S.; Tiedje, J. M. *J. Soil Sci.* **1990**, *41*, 1–4.
80. Christensen, S.; Christensen, B. T. *J. Soil Sci.* **1991**, *42*, 637–647.
81. Goodroad, L. L.; Keeney, D. R. *Can. J. Soil Sci.* **1984**, *64*, 187–194.
82. Christianson, C. B.; Cho, C. M. *Soil Sci. Soc. Am. J.* **1983**, *47*, 38–42.
83. Howarth, R. W.; Boyer, E. W.; Pabich, W. J.; Galloway, J. N. *Ambio* **2002**, *31*, 88–96.
84. Mosier, A. R. *Plant Soil* **2001**, *228*, 17–27.
85. Food and Agriculture Organization of the united nations, Rome 2008. ftp://ftp.fao.org/agl/agll/docs/cwfto11.pdf.
86. Galloway, J. N. *Environ. Poll.* **1998**, *102*, 15–24.
87. Campbell, N. A.; Reece J. B.; Mitchell L. G. *Biology*, 5th ed.; Benjamin Cummings: Menlo Park, 1999; pp 1028−1047.
88. Velthof, G. L.; Oenema, O. *Neth. J. Agic. Sci.* **1997**, *45*, 347–367.
89. Patra, A. K.; Abbadie, L.; Clays, A.; Degrange, V.; Grayston, S.; Guillaumaud, N.; Loiseau, P.; Louault, F.; Mahmood, S.; Nazaret, S.; Philippot, L.; Poly, F.; Prosser, J. I.; Le Roux, X. *Environ. Microbiol.* **2006**, *8*, 1005–1016.

90. Gu¨sewell, S.; Jewell, P. J.; Edwards, P. J. *Plant Soil* **2005**, *268*, 135–149.
91. Leriche, H.; Le Roux, X.; Gignoux, J.; Tuzet, A.; Fritz, H.; Abbadie, L.; Loreau, M. *Oecologia* **2001**, *129*, 114–124.
92. Lipson, D. A.; Schmidt, S. K. Seasonal changes in an alpine bacterial community in the Colorado Rocky Mountains. *Appl. Environ. Microbiol.* **2004**, *70*, 2867–2879.
93. Bardgett, R. D.; Wardle, D. A.; Yeates, G. W. *Soil Biol. Biochem.* **1998**, *30*, 1867–1878.
94. Louault, F.; Pillar, V. D.; Aufrere, J.; Garnier, E.; Soussana, J.-F. *J. Veg. Sci.* **2005**, *16*, 151–160.
95. Bullock, J. M.; Franklin, J.; Stevenson, M. J.; Silvertown, J.; Coulson, S. J.; Gregory, S. J.; Tofts, R. *J. Appl. Ecol.* **2001**, *38*, 253–267.
96. Whitehead, D. C. *Grassland nitrogen*; CAB International: Wallingford, 1995; pp 36−58.
97. De Klein, C. A. M.; Barton, L.; Sherlock, R. R.; Li, Z.; Littlejohn, R. P. *Aust. J. Soil Res.* **2003**, *41*, 381–399.
98. De Klein, C. A. M.; Smith, L. C.; Monaghan, R. M. *Agric. Ecosyst. Environ.* **2006**, *112*, 192–199.
99. IPCC. *Climate change: the Science of Climate Change*; Cambridge University Press: Cambridge, UK, 1995.
100. Petersen, S. O.; Lind, A. M.; Sommer, S. G. *Agric. Sci.* **1998**, *130*, 69–70.
101. Van Bruchem, J.; Shiere, H.; Van Keulen, H. *Livestock Prod. Sci.* **1999**, *61*, 145–153.
102. Van der Hoek, K. W. Proceedings of the 2nd International Nitrogen Conference on Science and Policy 2001. The scientificWorld1
103. Velthof, G. L.; Kuikman, P. J.; Oenema, O. *Biol. Fertil. Soils* **2003**, *37*, 221–230.
104. Petersen, S. O.; Regina, K.; Pollinger, A.; Rigler, E.; Valli, L.; Yamulki, S.; Esala, M.; Fabbri, C.; Syvasalo, E.; Vinther, F. P. *Agric., Ecosyst. Environ.*, *112*, 200–206.
105. Shepherd, T. G.; Saggar, S.; Newman, R. H.; Ross, C. W.; Dando, J. L. *Aust. J. Soil. Res.* **2001**, *39*, 465–489.
106. Gajri, P. R.; Arora, V. K.; Prihar, S. S. *Tillage for Sustainable Cropping*; Food Products Press: New York, 2002.
107. Bell, B. *Farm Machinery*, 4th ed.; Farming Press Books: Ipswich, 1996.
108. Jordan, V.; Leake, A. In *Managing Soil and Roots for Profitable Production*; HGCA Conference 2004.
109. El Titi, A., Ed.; *Soil Tillage in Agroecosystems*; CRC Press: Boca Raton, Fl, 2003.
110. Lal, R.; Reicosky, D. C.; Hanson, J. D. *Soil Tillage Res.* **2007**, *93*, 1–12.
111. Cunningham, M. H.; Chaney, K.; Bradbury, R. B.; Wilcox, A. *Ibis* **2004**, *146* (Suppl. 2), 192–202.
112. Holland, J. M. *Agric., Ecosyst. Environ.* **2004**, *103*, 1–25.
113. ECAF: European Conservative Agriculture Fedration, 2004. http://www.ecaf.org.
114. Gebhardt, M. R.; Daniel, T. C.; Schweizer, E. E.; Allmaras, R. R. *Science* **1985**, *230*, 625–629.

115. Ball, B. In *Agriculture: Energy Saving by Reduced Soil Tillage*; Bäumer, K., Ehlers, W., Eds.; EC Workshop, Gottingen, Luxembourg, 1987; pp 29−40.
116. Forristal, D.; Fortune, T. Teagasc National Tillage Conference Proceedings. www.teagasc.ie/publications/2003.
117. Grant, B.; Smith, W. N.; Desjardins, R.; Lemke, R.; Li, C. *Clim. Change* **2004**, *65*, 315–332.
118. Baggs, E. M.; Stevenson, M.; Pihlatie, M.; Regar, A.; Cook, H.; Cadish, G. *Plant Soil* **2003**, *254*, 361–370.
119. Li, C.; Frolking, S.; Butterbach-Bahl, K. *Clim. Change* **2005**, *72*, 321–338.
120. Grandey, A. S.; Loecke, T. D.; Parr, S.; Robertson, G. P. *J Environ. Qual.* **2006**, *35*, 1487–1495.
121. Liu, X. J.; Mosier, A. R.; Halvorson, A. D.; Zhang, F. S. *Plant Soil* **2006**, *280*, 177–188.
122. Aulakh, M. S.; Rennie, D. A.; Paul, E. A. *Soil Sci. Soc. Am. J.* **1984**, *48*, 790–794.
123. Bouwman, A. F. *Nutr. Cycling Agroecosyst.* **1996**, *46*, 53–70.
124. Six, J.; Ogle, S.; Breidt, F. J.; Contant, R. T.; Mosier, A. R.; Paustian, K. *Global Change Biol.* **2004**, *10*, 155–160.
125. Sundermeier, A. *Soil and Water Conservation Society 64th International Annual Conference*, Dearborn, MI, 50, 2009. http://www.swcs.org/en/conferences/past_annual_conferences/2009_annual_conference/.
126. Meisinger, J. J.; Hargrove, W. L.; Mikkelsen, R. L.; Williams J. R.; Benson, V. W. Proceedings of an International Conference, April 9–11, 1991, Jackson, TN; Soil and Water Conservation Society: Ankeny, IA, 1991; pp 57−68.
127. Parkin, T. B.; Kaspar, T. C.; Singer, J. W. *Plant Soil* **2006**, *289*, 141–152.
128. Potthoff, M.; Dyckmans, J.; Flessa, H.; Muhs, A.; Beese, F.; Joergensen, R. G. *Soil Biol. Biochem.* **2005**, *37*, 1259–1266.
129. Lupwayi, N. Z.; Clayton, G. W.; O'Donovan, J. T.; Harker, K. N.; Turkington, T. K.; Soon, Y. K. *Can. J. Soil Sci.* **2006**, *86*, 473–481.
130. Schoenau, J. J; Campbell, C. A. *Can. J. Plant Sci.* **1996**, *76*, 621–626.
131. Vigil, M. F.; Kissel, D. E. *Soil Sci. Soc. Am. J.* **1991**, *55*, 757–761.
132. Toma, Y.; Hatano, R. *Soil Sci. Plant Nutr.* **2007**, *53*, 198–205.
133. Akiyama, H.; Tsuruta, H. *J. Environ. Qual.* **2003**, *32*, 423–431.
134. Huang, Y.; Zou, J; Zheng, X; Wang, Y; Xu, X. *Soil Biol. Biochem.* **2004**, *36*, 973–981.
135. Velthof, G. L.; Oenema, O.; Van Beusichem, M. L.; Manning, W. J.; Dempster, J. P. *Environ. Pollut.* **1998**, *102*, 173–178.
136. Duxbury, J. W.; Bouldin, D. R.; Terry, R. E.; Tate, R. L., III. *Nature* **1982**, *298*, 462–464.
137. Eichner, M. *J. Environ. Qual.* **1990**, *19*, 272–280.
138. Steele, K. W.; Daniel, R. M.; Bonish, P. M.; O'Hara, G. Proceedings of the 19th technical conference of New Zealand Fertilizer Manufacturers, Auckland, New Zealand, 1983, pp 161−172.
139. Rochette, P.; Janzen, H. H. *Nutr. Cycling Agroecosyst.* **2005**, *73*, 171–179.
140. IPCC, 2006. *Intergovernmental Panel on Climate Change*; IPCC/ IGES, Hayama, Japan, 2006.

141. Houghton, J. T., Callander, B. A., Varney, S. K., Eds.; *Climate Change*, The Supplementary Report to the IPCC Scientific Assessment; Cambridge University Press: New York, 1992.
142. Kattenberg, A. F.; Giorgi, H.; Grassl, G. A.; Meehl, J. F. B.; Mitchell, R. J.; Stouffer, T.; Tokioka, A. J.; Weaver, Wigley; T. M. L.; et al. Climate models - Projection of future climate. In *Climate Change 1995. The Science of Climate Change. Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change*; Houghton, J. T., Meiro Filho, L. G., Callander, B. A., Harris, N., Kattenberg, A., Maskell, K., Eds.; Cambridge University Press: New York, 1996; Chapter 6, pp 285−357.
143. Addiscott, T. M. *Soil Sci.* **1983**, *34*, 343–353.
144. Scott, D. E.; Elliott, L. F.; Papendick, R. I.; Campbell, G. S. *Soil Biol. Biochem.* **1986**, *18*, 577–582.
145. Beauchamp, E. G.; Trevors, J. T.; Paul, J. W. *Adv. Soil Sci.* **1989**, *10*, 113–142.
146. Dueri, S.; Calanca, P. L.; Fuhrer, J. *Agric. Syst.* **2007**, *93*, 191–214.
147. Lu, X.; Cheng, G. *Soil Biol. Biochem.* **2009**, *41*, 1015–1021.
148. Clayton, H.; McTaggart, I. P.; Parker, J.; Swan, L.; Smith, K. A. *Biol. Fertil. Soils* **1997**, *25*, 252–260.
149. Hellebrand, H. J.; Kern, J.; Scholz, V. *Atmos. Environ.* **2003**, *37*, 1635–1644.
150. Waksman, S. A.; Gerretsen, F. C. *Ecology* **1931**, *12*, 33–60.
151. Abdalla, M.; Jones, M.; Williams, M. *Biol. Fert. Soils* **2010**, *46*, 247–260.
152. Kirschbaum, M. U. F. *Soil Biol. Biochem.* **1995**, *27*, 753–760.
153. Wennman, P.; Katterer, T. *J. Environ. Qual.* **2006**, *35*, 1135–1141.
154. Willams, E. J.; Hutchinson, G. L.; Feshsenfeld, F. C. *Global Biogeochem. Cycles* **1992**, *6*, 351–388.
155. Li, C.; Frolking, S.; Frolking, T. A. *Geophys. Res.* **1992**, *97*, 9759–9776.
156. Parton, W. J; Ojima, D. S.; Cole, C. V.; Schimel, D. S. Quantitative Modelling of Soil Forming Processes; Soil Science Society of America, Inc.: Madison, WI, **1994**; pp 147−167.
157. Del Grosso, S. J.; Ojima, D. S.; Parton, W. J.; Mosier, A. R.; Peterson, G. A.; Schimel, D. S. *Environ. Pollut.* **2002**, *116*, S75–S83.
158. DelGrosso, S. J.; Ojima, D. S.; Parton, W. J.; Stehfest, E.; Heistemann, M.; DeAngelo, B.; Rose, S. *Global Planet Change* **2009**, *67*, 44–50.
159. Li, C; Narayanan, V.; Harriss, R. *Global Biogeophys. Cycles* **1996**, *10*, 297–306.
160. Li, C.; Zhuang, Y.; Cao, M.; Crill, P.; Dai, Z.; Frolking, S.; Moore, B.; Salas, W.; Song, W.; Wang, X. *Nutr. Cycling Agroecosyst.* **2001**, *60*, 159–175.
161. Smith, W. N.; Grant, B. B.; Desjardins, R. L.; Worth, D.; Li, C.; Boles, S. H.; Huffman, E. C. *Agric. Ecosyst. Environ.* **2010**, *136*, 301–309.
162. Kesik, M.; Bruggemann, N.; Forkel, R.; Kiese, R.; Knoche, R.;Li, C.; Seufert, G.; Simpson, D.; Butterbach-Bahl, K. *J. Geophys. Res.* 2006111, G02018, doi:10.1029/ 2005JG000115, 2006.
163. Abdalla, M.; Wattenbach, M.; Smith, P.; Ambus, P.; Jones, M.; Williams, M. *Geoderma* **2009**, *151*, 327–337.

164. Abdalla, M; Jones, M; Yeluripati, J; Smith, P.; Burke, J.; Williams, M. *Atmos. Environ.* **2010**, *44*, 2961–2970.
165. Bouwman, A. F. In *Soil and the Greenhouse Effects*; Bouwman, A. F., Ed.; Wiley: Chichester, U.K., 1990; pp 61−127.
166. De Klein, C. A. M.; Sherlock, R. R.; Cameron, K. C.; Van der Weerden, T. *J. R. Soci. N. Z* **.2001**, *31*, 543–574.
167. Hendriks, C. A.; De Jager, D.; Blok, K. *Interim report, by order of the DGXI, EC, ECOFYS*; Utrecht, The Netherlands, 1998.
168. Erisman, J. W.; van Grinsven, H.; Leip, A.; Mosier, A.; Bleeker, A. *Nutr. Cycling Agroecosyst.* **2010**, *86*, 211–223.
169. Van Groenigen, J. W.; Velthof, G. L.; Oenema, O.; van Groenigen, K. J.; van Kessel, C. *Eur. J. Soil Sci.* **2010**, *61*, 903–913.
170. Brink, J. C.; Hordijk, L.; Van Ireland, E. C.; Kroeze, C. *Workshop of Assessing the Ancillary Benefits and Costs of Greenhouse gas Mitigation Strategies*; 27-29 March 2000, Washington, DC.
171. Wagner-Riddle, C. A.; Furon, N. L.; McLaughlin, I.; Lee, J.; Barbeau, S.; Jayasundara, G.; Parkin, P.; von Bertoldi; Warland, J. *Global Change Biol.* **2007**, *13*, 1722–1736.
172. Mosier, A. R.; Klemedtsson, L. In *Methods of soil analysis. Part 2. Microbiological and Biochemical Properties*; Weaver, R. W., Angle, S., Bottomley, P., Bezdicek, D., Smith, S., Tabatabai, A., Wollum, A., Eds.; Soil Science Society of America, Inc.: Madison, WI, 1994; pp 1047−1065.
173. Merino, P.; Estavillo, J. M.; Graciolli, L. A.; Pinto, M.; Lacuesta, M.; Muñoz-Rueda, A.; Gonzalez-Murua, C. *Soil Use Manag* **2002**, *18*, 135–141.
174. Di, H. J.; Cameron, K. C. *Soil Use Mang.* **2003**, *19*, 284–290.
175. Stevens, R. J.; Laughlin, R. J.; Mosier, R.; Abrahamsen, G.; Bouwman, L.; Bockman, O.; Drange, H.; Frolking, S.; Howarth, R.; Kroeze, C.; Oenema, O.; Smith, K.; Bleken, M. A. *Nutr. Cycl. Agroecosyst.* **1998**, *52*, 131–139.
176. Van der Weerden, T. J.; Sherlock, R. R.; Williams, P. H.; Cameron, K. C. *Biol. Fert. Soils* **1999**, *30*, 52–60.

Chapter 19

Assessing the Environmental Impact of Agriculture in Europe: The Indicator Database for European Agriculture

Adrian Leip[*]

European Commission, Joint Research Centre,
Institute for Environment and Sustainability
[*]E-mail: adrian.leip@jrc.ec.europa.eu

The Indicator Database for European Agriculture (IDEAg) has been developed to provide a means of assessing consistently the impact of agricultural activities on the environment in Europe. It assembles data from four models running at high spatial resolution for the countries in the European Union (EU27): CAPRI-SPAT, MITERRA-CAPRI, DNDC-EUROPE and the DNDC-CAPRI meta-model. IDEAg combines the strength of these models while offering new possibilities for calculating marginal emission factors or integrating agriculture with other economic sectors. We discuss recent applications of the IDEAg, including the development of stratified N_2O emission factors and nitrogen budgets, and the assessment of the intensification effect of growing crops for the production of biofuels.

Introduction

Agricultural activities are inextricably linked to environmental services of the land it occupies and to the environmental consequences of the emissions to the atmosphere and the deteriorated water quality they cause. Dedicated models and tools have been developed to assess the impact of agriculture on climate change, groundwater pollution, air pollution, and biodiversity and to help devising mitigation measures. Yet, tackling environmental risks individually bears the risk of pollution swapping, thereby revealing the need for integrated assessment tools. The Indicator Database for European Agriculture (IDEAg) has been developed to

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

provide a means of assessing consistently the impact of agricultural activities on the environment in Europe.

Currently, the focus of the applications is on the assessment of emissions of reactive nitrogen to the environment and on radiative active trace gases. The paper will discuss the modeling framework using examples of recent applications including the estimation of regional emission factors for N_2O fluxes from agricultural soils in Europe (*1*), the development of nitrogen budgets and nitrogen indicators for European agriculture (*2*), and the assessment of the intensification effect of growing crops for the production of biofuels (*3*).

Methods

The Indicator Database for European Agriculture (IDEAg) assembles data that are generated within the CAPRI-DNDC modelling framework (CDMF). The CDMF consists of four main modelling tools that combine and process data drawn from two European databases. These databases are (i) the regional database for agriculture obtained from the CAPRI (Common Agricultural Policy Regional Impact) model which includes also data for nitrogen losses calculated by MITERRA-CAPRI (*4*) and (ii) a GIS environmental database for EU27 (*5*).

The IDEAg model-interface is the core of the CDMF and assimilates various data streams into a consistent and comprehensive database. The data streams must be available at the same spatial definition, which for the CDMF are about 200,000 spatial units at a 1 km x 1 km pixel grid for EU27. However, no restriction is put on the the scientific approach with which environmental indicators are estimated. Thus, within the CDMF, data from simple activity-data/emission-factor models are combined with results from empirical models and statistical models. Land use, farm management and environmental indicators are disaggregated from the regional CAPRI database to a gridded map with the CAPRI-Spat tool (*6*, *7*); nitrogen fluxes were also estimated with the process-based DNDC-EUROPE model for nutrient turnover in agricultural soils (*5*, *8*), with a feed-back to the IDEAg model interface through the DNDC-CAPRI meta-models (*9*). The linkages between the tools are shown in Figure 1.

Input Data

The CAPRI Regional Database

The CAPRI (Common Agricultural Policy Regionalised Impact) model is a global economic model for agriculture with a regionalized focus for Europe [see (*4*)]. Its database comprises times series of mutually consistent national and regional data on agricultural activities (crop acreages and animal numbers), productivities (e.g. crop and milk yields, and carcass weights) and farm input (e.g. mineral fertilizer and manure nitrogen application rates per crop). Statistical data are mainly obtained from EUROSTAT, however the data are examined for consistency and completeness. Identified data gaps are filled by means of an automated algorithm and data inconsistencies are corrected.

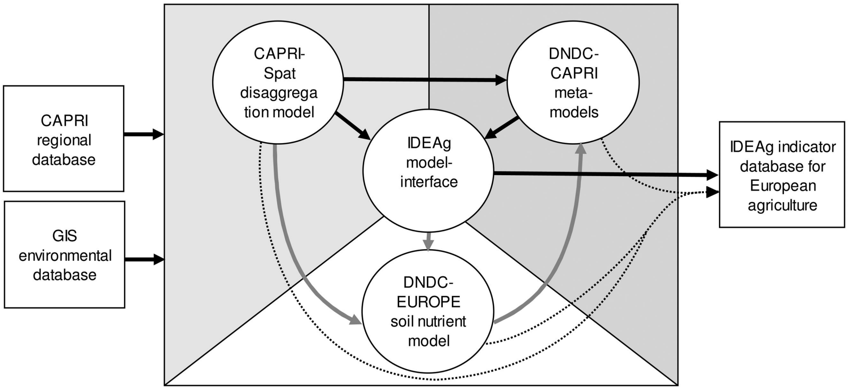

CAPRI regional database
GIS environmental database
CAPRI-Spat disaggregation model
DNDC-CAPRI meta-models
IDEAg model-interface
DNDC-EUROPE soil nutrient model
IDEAg indicator database for European agriculture

Figure 1. Schematic representation of the CAPRI-DNDC modelling framework (CDMF) and the Indicator Database for European Agriculture (IDEAg). The solid black lines show the main data flow to the IDEAg through the IDEAg model interface, but information obtained from the various models directly is stored as well, as shown by dotted lines. The grey solid lines indicate the feedback loop through the DNDC-EUROPE process-based model and the DNDC-CAPRI meta-models.

Physical market balances are calculated for both total biomass and nitrogen. Nitrogen losses to the atmosphere and the hydrosphere are calculated following the approach of the MITERRA-EUROPE model (*10*, *11*), including gaseous losses and leaching from housing and manure management as well as losses upon soil application. GHG fluxes are calculated using IPCC methodology (*12*, *13*). The data have recently been used to calculate additional nitrogen indicators such as nitrogen surplus and nitrogen use efficiencies for soil, land, and farm-N budgets (*2*).

The GIS Environmental Database

As a spatial calculation unit we use the definition of the "Homogeneous Spatial Mapping Unit (HSMU)" given in Leip *et al.* (*5*). Shortly, a HSMU is defined by the land cover class [Corine 2000, (*14*)], a soil mapping unit (*15*), slope on the basis of data from the Catchment Characterisation and Modelling DEM 250 (*16*), and an administrative region at the so-called NUTS2-level (*17*). For Europe, we defined 206000 HSMUs with a mean area by country ranging from 7 km^2 (Slovenia) to 94 km^2 (Finland) (*5*).

Main environmental data include top-soil characterization (pH, texture, bulk density and initial soil organic carbon content) meteorological information (minimum and maximum daily temperature, and daily precipitation), and information on nitrogen deposition. Soil information for agricultural land is derived from raster data available from the European Soil Database (*18*, *19*) as described by Leip *et al.* (*1*). Meteorological data are interpolated from daily

MARS grid weather at coarse resolution (*20*) and montlhy ATEAM/CRU data at 10'x10' spatial resolution (*21*) as described in Orlandini and Leip (*22*).

Modelling Tools

The CAPRI-Spat Disaggregation Model

CAPRI-SPAT takes agronomic information from the regional CAPRI database and estimates their distribution over the HSMUs within each region. The procedure is described in detail in Leip et al. (*5*) and Kempen et al. (*6*). The model generates spatially explicit datasets input for process-based models such as land use (acreage) and livestock density (as livestock units), yield for each crop cultivated in a calculation unit, application rates of mineral fertilizer nitrogen and manure nitrogen for each spatial unit and crop, the amount of manure deposited on grassland during grazing, and the C/N ratio of applied manure. Maps are also created for environmental and socio-economic indicators such as GHG or N-gas (NH_3, NO_x, N_2) emissions from agricultural activities, composition of human diets, and GHG emissions from waste water treatment systems (*5*, *23*).

Briefly, crop shares (mean and variance) are estimated into the spatial units with distance-weighted logit-models that have been developed on the basis of ground-truth observations from a Land Use/Cover Area Frame Statistical Survey (*24*) for each land cover class in the Corine 2000 database (*14*). Consistency with regional totals is achieved using the Highest Posterior Density technique (*25*). The disaggregation of crop-yield makes use of information on potential yield (*26*) and irrigation (*27*). Nitrogen applications are estimated on the basis of nitrogen requirements including estimated over-fertilization rates, and nitrogen availability as manure, from atmospheric deposition and biological nitrogen fixation, and as mineral fertilizer.

The DNDC-EUROPE Model

The Denitrification-Decomposition model (DNDC) (*8*, *28–30*) is a process-oriented biogeochemistry model for agro-ecosystems which was originally developed for application at field level, but subsequently developed to be applied at a regional scale. It is comprised of two components which integrate ecological drivers (e.g., climate, soil, vegetation, etc.), soil environmental factors (e.g., texture, pH, etc.) and anthropogenic drivers (land use, tillage, N-application) to calculate the state of the soil-plant system and organic carbon mineralization. The second component focuses on the calculations of the major processes involved in the exchange of GHGs with the atmosphere, i.e. nitrification, denitrification and fermentation.

The model has been tested against numerous field data sets of nitrous oxide (N_2O) emissions and soil carbon dynamics (*31*). DNDC has been widely used for regional modelling studies in the USA (*32*), China (*33*, *34*), New Zealand (*35*), India (*36*) and Europe (*1*, *37–40*).

The DNDC-CAPRI Meta-Model

The DNDC-CAPRI meta-model is a set of regression models simulating the main fluxes of nitrogen from agricultural soils for 11 crops or crop-groups at the level of the HSMUs. The simulated fluxes are nitrogen leaching, soil organic nitrogen mineralization and emissions of NO_x, N_2O, NH_3 and N_2, as well as nitrogen uptake by the crops and total nitrogen losses. The model is calibrated with a large pool of results obtained for simulations with the DNDC-EUROPE model and thus mimics the annual results of the process-based model explaining most of the variability observed in the data pool (*9*).

The DNDC-CAPRI meta-model serves two main purposes, i.e. improve the consistency between CAPRI-Spat and DNDC-EUROPE data by estimating the potential crop yield for each spatial unit, and accelerating the simulation of annual fluxes of reactive nitrogen allowing, for example, the quantification of marginal emission factors (*9*). Crop yield is simulated dynamically by the DNDC-model using the potential yield as input. The potential yield is a function of the planted variety of the crop and its interaction with the site-specific conditions (soil and climate) in the absence of water and nutrient stress. The yield-gap as a result of the above-mentioned stresses is simulated dynamically on a daily basis, driven by weather and farm management. A good estimate of the potential yield is essential to match simulated and statistical (downscaled) yield and to minimize the bias in estimated nitrogen losses when combining (statistical) N-input with simulated crop uptake.

The Interface for European Agricultural Indicators

The IDEAg model interface (IDEAg-MI) fulfills three important tasks. First, it combines the data streams from the different models and and selects for each indicator the most appropriate data source. Table 1 shows the indicators related to the fate of nitrogen applied to agricultural soils. Nitrogen input is obtained from CAPRI-Spat and includes the application of mineral fertilizer and manure nitrogen, the deposition of manure by grazing animals, atmospheric deposition and biological N-fixation. Nitrogen losses are estimated both by the MITERRA-EUROPE model, as implemented in CAPRI and downscaled with CAPRI-Spat as well as from the DNDC-CAPRI meta-model.

Second, the IDEAg-MI ensures that for each landuse/spatial unit combination a closed N-budget is achieved. N additions by mineral fertilizer, manure, biological fixation and atmospheric deposition (N-input), N removal during harvest (N-harvest) and thus also total net N-losses from the soil-crop continuum are given from CAPRI-SPAT. They are consistent with regional and national agricultural statistics (or simulated projections). The individual terms for N-losses and N-mineralization are obtained with independent models and will usually result in a total loss different from the one obtained from CAPRI-SPAT.

Table 1. Elements of the N-fluxes in the IDEAg

Flux	*Source of information*
N-input	CAPRI-SPAT
N-harvest	CAPRI-SPAT
NH_3	MITERRA-CAPRI
NO	DNDC-CAPRI meta-model
N_2O	DNDC-CAPRI meta-model
N-runoff	MITERRA-CAPRI
N-leaching	DNDC-CAPRI meta-model
N-mineralization	DNDC-CAPRI meta-model
N_2	DNDC-CAPRI meta-model

Thus, it is required to adjust the individual loss-terms and this is done on the basis of the assumed scientific robustness of the data:

- MITERRA-CAPRI (*10*, *11*) is considered to be a robust empirical estimate of annual fluxes of NH_3 and N-run-off; the DNDC model has been calibrated and validated in particular for N_2O and NO_x fluxes, which were often at the focus of the studies and for which most experimental data were available. Thus, NH_3 fluxes and N-runoff from CAPRI-MITERRA, as well as N_2O and NO_x fluxes from the DNDC-CAPRI meta-model are considered to be good estimates and are not subject to adjustments.
- N_2 fluxes from DNDC are likely to be underestimated while NH_3 fluxes are likely to be overestimated (*9*). Leip *et al.* (*5*) found a N_2/N_2O ratio of about 2 for simulations with DNDC-EUROPE, while from a global analysis a ratio of about 10 seems more likely (*41*, *42*). Therefore, if NH_3 fluxes from CAPRI-MITERRA are smaller than estimated by the DNDC-CAPRI meta-model, the difference is assumed to be emitted as N_2.
- Estimated mineralization rate of organic nitrogen are strongly affected by soil data used and are regarded to be uncertain (*5*). Rates of N-mineralization larger than 25 kg N ha^{-1} yr^{-1} are assumed to be unlikely [see e.g. (*43*)] and the difference to 25 kg N ha^{-1} yr^{-1} is reduced by 85%.
- Only in case that these adjustment were not sufficient to match CAPRI-SPAT and IDEAg-MI, N-losses are scaled involving N_2-fluxes and N-leaching and N-mineralization and in a few cases also N_2O and NO_x fluxes.

Third, the IDEAg-MI allows seamless integration of additional information and calculation of additional nitrogen fluxes.

Applications

The CAPRI-DNDC modelling framework has been applied in the past few years for applications of various purposes.

Simulation of N_2O Fluxes

N_2O fluxes from agricultural soils are strongly dependent on local conditions, in particular soil, weather and farm management. Skiba and Smith (*44*) suggested that differences in N_2O emissions measured for different crops are partly caused by the fact that they are grown on different locations and managed differently. Thus obtaining good estimates of the spatial distribution of crop shares and farm management is a prerequisite for realistic simulations of N_2O fluxes. Erisman et al. (*45*) report from results obtained with the CAPRI-DNDC modelling framework on rape seed and sugar beet used for biofuel productions that high emissions from rape seed are influenced by the soils on which they were estimated. This leads to a break-even point of below 250 kg N ha^{-1} yr^{-1} for some regions. The break-even point indicates the amount of fertilizer application, above which no greenhouse gas savings are expected if the crop is used as biofuel. Relatively low N-input from sugar beet per ton of harvested biomass makes ethanol from sugar beet more competitive in terms of N_2O fluxes (*45*). This needs to be balanced by larger energy requirement for processing of sugar beet ethanol and lower credits of by-products (*46*).

Estimates of N_2O fluxes are the most uncertain element in national GHG inventories submitted to the UNFCCC (*47*, *48*). Most countries are relying on the IPCC default emission factor because the experimental data needed to derive robust national emission factors are not available. Also, estimates of the uncertainty are often subjective (*48*). The accuracy of GHG inventories can only be increased if the uncertainty of estimates of N_2O fluxes from agricultural soils is reduced. Leip et al. (*1*) show that simulations with the DNDC-EUROPE model within the model-framework can be used to develop stratified N_2O emission factors for countries in Europe. Their results indicate that such an approach leads to differentiated emission factors that most likely are associated with reduced uncertainties compared to those reported in the national GHG inventories. The application of such factors in official reports however necessitates additional efforts in quantifying the structural error or bias of the simulation model [see e.g. (*49*)].

Nitrogen Budgets

The nitrogen cascade poses multiple threats to the environment and human health and a cost-efficient portfolio of measures requires the consideration of antagonistic and synergistic effects (*50*). Such an assessment obviously must rely on impact assessment using consistent methodologies. In Europe, agriculture contributes to total emissions of reactive nitrogen at about 95% of NH_3 emissions and 3% of NO_x emissions, with total emissions of NO_x (3.5 Tg N) being slightly higher than total NH_3 emission (3.2 Tg N) (*23*). These data have been obtained

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

by combining results from the IDEAg with emission estimates from other sectors, i.e. industry and energy, transport, waste, and from ecosystems, i.e. forests and inland and coastal waters.

N- losses from agriculture in Europe are related to a low N-use efficiency of only about 30%, if calculated at farm-scale boundaries (*2*). Obviously, large variability between European countries was found and the highest explanatory strength was found in the significance of atmospheric deposition in the total N-input, which can be interpreted as an indicator for extensive agriculture, and the specialization for animal products. In view of a comprehensive assessment of nitrogen cycling through the European society and environment, information on human consumption of proteins and their fate in waste-water treatment systems has been added to the IDEAg. N_2O emissions from waste-water treatment systems are estimated to amout to about 20 Gg N yr^{-1}, making a relatively small contribution to overall N_2O fluxes of about 2% for the year 2000.

Overall, Leip et al. (*23*) estimate that agriculture contributes about 45% to total emissions of reactive nitrogen to the atmosphere, and 70% to the emissions towards the hydrosphere.

Intensification of Crop Production

One of the major future problems is to ensure food security while at the same time not jeopardizing other services of the land to our disposition, i.e. climate regulation, genetic resources, and provision of fibre and fuel, to name just a few (*51*). With a growing population and increasing demand, for example, on bio-energy, a crucial question is how much land can be taken into production without affecting existing areas of high nature value, and how much biomass can be made available by increasing productivity on land which is already under cultivation [see e.g. (*52*)]. It is a difficult task to predict future yield increases as it is unclear whether or not the 'green revolution' can continue (*53*).

The DNDC-CAPRI meta-model can only assess the environmental impact related to yield changes that are achieved by increasing nitrogen additions to the soil. Britz and Leip (*9*) evaluated the environmental cost of intensification for rape seed and wheat cultivation at one virtual location with average conditions in Europe by simulating the fluxes of reactive nitrogen at different rates of application of mineral fertilizer. At each application rate, the system is 'shocked' with one additional kilogram of nitrogen and the difference in fluxes of reactive nitrogen with respect to the un-shocked simulations are reported as marginal nitrogen fluxes at the corresponding N-application rate.

Figure 2 shows marginal fluxes of N_2O and NO_x as well as marginal uptake of nitrogen into the biomass and nitrogen leaching rates for wheat, rape seed and sugar beet for EU27. In the figure, data are not calculated at representative conditions, but rather as an average of marginal rates simulated at 1900, 800 and 900 randomly chosen spatial units across Europe for the three crops, respectively. The pattern is similar to the figures presented by Britz and Leip (*9*) with strong reductions of additional N-uptake for high N-application rates. These are counterbalanced by increasing losses to the environment, with nitrogen leaching becoming the major pathway of N-additions in particular for rape seed. NO_x

fluxes are relatively constant over the range of N-applications assessed, while the N_2O factor increases at low N-application rates to stabilize or even decrease at high N-application rates. N_2O fluxes are relatively high, if compared to global averages and also to European values as simulated with the DNDC-EUROPE model (*1*), averaged over all crops. However, Skiba and Smith (*44*) report emission factors for sugar beet and rape seed between 1.5% and 4.1%, and 1.4% and 2.5%, respectively, in a Scottish study. Freibauer and Kaltschmitt (*54*) conclude that N-rich crop residues might lead to high N_2O fluxes in crops such as rape seed. Despite the uncertainty that surrounds these emission factor estimates, there are conclusions to be drawn. (i) When talking about the environmental impact of intensification, the N_2O emissions caused by additional N-input are often higher than the average emission factor suggests. (ii) Marginal N_2O fluxes per kilogram of produced biomass increase significantly at high nitrogen doses as marginal biomass production decreases. It will be the task of careful evaluations to find the level at which the environmental cost of intensification exceeds those generated by higher land needs and associated (indirect) land use change effects.

Discussion

NH_3 and N_2 fluxes are the least constrained ones in the DNDC model. In both cases, flux measurements are very expensive and only few datasets exist. From over 80 studies available, most of them are focusing on N_2O fluxes [e.g., (*55*)] and CH_4 [e.g., (*56*)], several on C sequestration rates [e.g., (*31*)] and some on NO fluxes [e.g., (*57*)] and N-leaching [e.g., (*32*)]. Parameterization of NH_3 fluxes is based on short-term flux measurements following fertilizer application in rice paddies in China (*8*). Britz and Leip (*9*) therefore conclude on the basis of a comparison with other large-scale estimates of NH_3 emissions, that NH_3 fluxes in DNDC and thus also in the DNDC-CAPRI meta-model are likely to be overestimated. The N_2:N_2O ratios in the simulated fluxes of the DNDC-CAPRI meta-model on the other hand are relatively narrow [see e.g. (*5*)] if compared with a likely global average N_2:N_2O ratio around 10. This suggests that N_2 fluxes are quantified as a “residual” N-loss and that over-estimated NH_3 losses might likely be the reason for under-estimated N_2-losses. In the IDEAg-MI, we therefore considered the NH_3 flux estimates calculated within the CAPRI modelling systems according to the methodology developed by Velthof et al. (*11*) as a better estimate for NH_3 fluxes and assumed that the difference in the estimates will be lost as N_2.

Mineralization of soil organic matter critically depends on the assumed initial conditions of the soil. As discussed in Leip et al. (*5*), soil organic matter estimates at the European level are very uncertain and therefore also the estimates of SOM mineralization rates obtained with the DNDC-CAPRI meta-model are not well constrained. In order to maintain a closed soil N-budget, we use the estimates of N-mineralization to partly close gaps in the N-balance. Obviously, the present version of the IDEAg-MI is therefore not fit to deliver robust estimates of changes in soil organic matter and related changes in the soil C and N pools. Hence, the improvement of the initialization of soil organic carbon for DNDC-EUROPE simulation is of highest priority for the development of the next version of the DNDC-CAPRI meta-model.

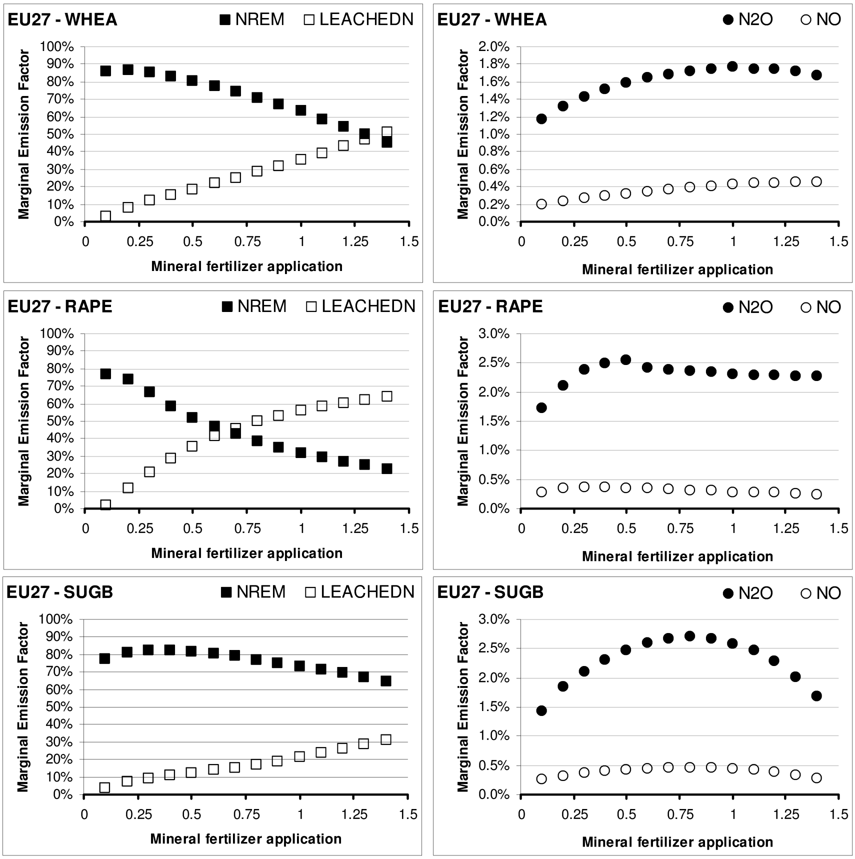


Figure 2. Marginal Emission Factors (MEFs) for Nitrogen uptake in biomass (NREM) and nitrogen leaching (LEACHEDN) in the left panel and N_2O and NO_X fluxes in the right panel. MEFs are calculated for wheat, rape seed and sugar beet. The x-axis gives application of mineral fertilizer relative to current management practices as estimated in the IDEAg (average of simulated spatial units). For EU27, this is 165, 110, and 205 kg N ha^{-1} yr^{-1} for wheat, rape seed, and sugar beet, respectively.

A major challenge of the IDEAg-MI is to find a compromise between the use of individual N-flux estimates obtained with tools that are believed to represent their respective state-of-the art on one hand and the constraints given by the applications requiring (i) scale-consistency of the data from the level of the HSMU to the regional and national scales, (ii) a closed N-budget at each of these scales, and (iii) consistency of major components of the N-budget (yield defining N-removal, N-input with mineral fertilizer and manure) with official statistics at the regional level. The rules developed for IDEAg are based on the observations discussed above and expert judgement. Even though they contain some subjective component, they are able to fulfil all the requirements described and ensure thus that the IDEAg combines the strengths of CAPRI-SPAT, MITERRA-CAPRI, and DNDC-EUROPE in a seamless and complementary way. Process-based models are powerful tools to investigate mitigation scenarios or extrapolate flux estimates over larger areas, if additional observational data become too expensive. However, with increasing complexity of the models additional accuracy for one flux-term is often not matched by the accuracy of other terms. The IDEAg framework assimilates the strong components of models of different types, and potentially also field data, to overcome this problem.

Conclusions

The Indicator Database for European Agriculture (IDEAg) is a database that contains information from various data streams, integrated and made consistent with the IDEAg model interface. As the IDEAg framework combines the strength of different models we believe that its concept can be useful for a variety of applications. These include the development of marginal emission factors to assess the impact of intensification and extensification, the development of regional spatially explicit nitrogen budgets, or the integration of agricultural indicators into a larger framework. The first version of the IDEAg model interface makes use of the CAPRI-SPAT to estimate N-input to agricultural soils and N-uptake by crops, CAPRI-MITERRA model to estimate NH_3 emissions and run-off of nitrogen, and the DNDC-CAPRI meta-model to estimate other losses of reactive nitrogen. In future versions, some of these flux terms might be replaced by better model approaches when they become available.

References

1. Leip, A.; Busto, M.; Winiwarter, W. Developing spatially stratified N2O emission factors for Europe. *Environ. Pollut.* **2011**, *in press*.
2. Leip, A.; Britz, W.; De Vries, W.; Weiss, F. Farm, Land, and Soil nitrogen budgets for Agriculture in Europe calculated with CAPRI. *Environ. Pollut.* 2011**,** *in press*.
3. Leip, A.; Britz, W. Estimation of the marginal environmental impact of rapeseed production in Europe. 2009, *presentation at the 17th European Biomass Conference and Exhibition, Hamburg 2009.*
4. Britz, W.; Witzke, H.-P. *CAPRI Model Documentation 2008: Version 2*; Institute for Food and Resource Economics, University of Bonn: Bonn, 2008.
5. Leip, A.; Marchi, G.; Koeble, R.; Kempen, M.; Britz, W.; Li, C. Linking an economic model for European agriculture with a mechanistic model to estimate nitrogen and carbon losses from arable soils in Europe. *Biogeosciences* **2008**, *5* (1), 73–94.
6. Kempen, M.; Heckelei, T.; Britz, W.; Leip, A.; Koeble, R.; Marchi, G. *Computation of a European Agricultural Land Use Map – Statistical*

Approach and Validation; Institute for Food and Resource Economics, University of Bonn: Bonn, 2007; Vol. Technical Paper.

7. Britz, W.; Verburg, P. H.; Leip, A. Modelling of land cover and agricultural change in Europe: combining the CLUE and CAPRI-Spat approaches. *Agric., Ecosyst. Environ.* 2010**,** *online*.
8. Li, C. Modeling trace gas emissions from agricultural ecosystems. *Nutr. Cycl. Agroecosyst.* **2000**, *58*, 259–276.
9. Britz, W.; Leip, A. Development of marginal emission factors for N losses from agricultural soils with the DNDC-CAPRI meta-model. *Agric. Ecosyst. Environ.* **2009**, *133* (3-4), 267–279.
10. Oenema, O.; Witzke, H.-P.; Klimont, Z.; Lesschen, J. P.; Velthof, G. Integrated assessment of promising measures to decrease nitrogen losses from agriculture in EU-27. *Agric., Ecosyst. Environ.* **2009**, *133*, 280–288.
11. Velthof, G.; Oudendaag, D.; Witzke, H.-P.; Asman, W. A. H.; Klimont, Z.; Oenema, O. Integrated assessment of nitrogen emissions from agriculture in EU-27 using MITERRA-EUROPE. *J. Environ. Qual.* **2009**, *38*, 402–417.
12. Pérez, I. *Greenhouse Gases: Inventories, Abatement Costs and Markets for Emission Permits in European Agriculture. A Modelling Approach*; Lang, P.; Europäischer Verlag der Wissenschaften: Frankfurt am Main, 2005; Vol. 3184.
13. Weiss, F.; Leip, A. Methodology for quantification of greenhouse gas and ammonia emissions from the livestock sector in EU27. In *Evaluation of the livestock sector's contribution to the EU greenhouse gas emissions (GGELS) -final report*; Leip, A., Weiss, F., Wassenaar, T., Perez, I., Fellmann, T., Loudjani, P., Tubiello, F., Grandgirard, D., Monni, S., Biala, K., Eds.; European Commission, Joint Research Centre, 2010.
14. European Topic Centre on Terrestrial Environment, *Corine land cover database (Version 12/2000)*; 2000.
15. European Commission, *European Soil Database (version V2.0)*; European Commission, Directorate General Joint Research Centre, Institute for Environment and Sustainability, 2004; Vol. CD-ROM EUR 19945 EN, March 2004.
16. CCM - Catchment Characterisation and Modelling DEM 250, *EuroLandscape/Agri-Environment Catchment Characterisation and Modellig Activity*. Land Management Unit, Institute for Environment and Sustain-ability, EC-Joint Research Centre. 250 Meter DEM, compiled on the basis of data acquired from data providers and national mapping agencies over Europe for internal use, 2004.
17. EUROSTAT, *The Geographic Information System of the European Commission (GISCO) reference database: Version: 07/2003*; Statistical Office of the European Communities: Brussels, 2003.
18. ESBD. European Soil Database v.2.0 2006. http://eusoils.jrc.ec.europa.eu/data.html.
19. Jones, R. J. A.; Hiederer, R.; Rusco, E.; Montanarella, L. Estimating organic carbon in the soils of Europe for policy support. *Eur. J. Soil Sci.* **2005**, *56* (5), 655–671.

20. Orlandi, S.; Van der Goot, E. *Technical description of interpolation and processing of meteorological data in CGMS*; European Commission, DG JRC, Agrifish Unit, 2003.
21. Mitchell, T. D.; Carter, T. R.; Jones, P. D.; Hulme, M.; New, M. *A comprehensive set of high-resolution grids of monthly climate for Europe and the globe: the observed record (1901-2000) and 16 scenarios (2001-2100)*; Tyndall Centre for Climate Change Research, 2004; Vol. Working Paper 55.
22. Orlandini, L.; Leip, A. A high-resolution dataset of European daily weather from 1990-2000 for applications with ecosystem models. 2008; Vol. NitroEurope IP Open Science Conference - Reactive Nitrogen and the European Greenhouse Gas Balance. 20.-21. February, 2008, Ghent.
23. Leip, A.; Achermann, B.; Billen, G.; Bleeker, A.; Bouwman, L.; de Vries, W.; Dragosits, U.; Döring, U.; Fernall, D.; Geupel, M.; Johnes, P.; Le Gall, A. C.; Monni, S.; Nevečeřal, R.; Orlandini, L.; Prud'homme, M.; Reuter, H.; Simpson, D.; Seufert, G.; Spranger, T.; Sutton, M.; van Aardenne, J.; Voss, M.; Winiwarter, W. Integrating nitrogen fluxes at the European scale. In *European Nitrogen Assessment*; Sutton, M., Howard, C., Erisman, J. W., Billen, G., Bleeker, A., van Grinsven, H., Grennfelt, P., Grizzetti, B., Eds.; Cambridge University Press: Cambridge, UK, 2011; pp 345−376.
24. European Commission, *The Lucas survey. European statisticians monitor territory. Theme 5: Agriculture and fisheries*; Office for Official Publications of the European Communities, Luxembourg, 2003; p 24.
25. Heckelei, T.; Mittelhammer, R. C.; Britz, W. A Bayesian Alternative to Generalized Cross Entropy Solutions to Underdetermined Models. Contributed paper presented at the 89th EAAE Symposium "Modelling agricultural policies: state of the art and new challanges", February 3−5, Parma, Italy, 2005.
26. Genovese, G.; Baruth, B.; Royer, A.; Burger, A. Crop and yield monitoring activities - MARS STAT action of the European Commission. *Geoinformatics* **2007**, *10* (4), 20–22.
27. Siebert, S.; Döll, P.; Hoogeveen, J.; Faures, J.-M.; Frenken, K.; Feick, S. Development and validation of the global map of irrigation areas. *Hydrol. Earth Syst. Sci.* **2005**, *9*, 535–547.
28. Li, C.; Frolking, S.; Frolking, T. A. Model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity. *J. Geophys. Res.* **1992**, *97* (D9), 9759–9776.
29. Li, C. Quantifying greenhouse gas emissions from soils: Scientific basis and modeling approach. *Soil Sci. Plant Nutr.* **2007**, *53* (4), 344–352.
30. Giltrap, D. L.; Li, C.; Saggar, S. DNDC: A process-based model of greenhouse gas fluxes from agricultural soils. *Agric., Ecosyst. Environ.* **2010**, *136* (3-4), 292–300.
31. Li, C.; Frolking, S.; Butterbach-Bahl, K. Carbon sequestration in arable soils is likely to increase nitrous oxide emissions offsetting reductions in climate readiative forcing. *Clim. Change* **2005**, *72* (3), 321–338.
32. Tonitto, C.; David, M. B.; Li, C.; Drinkwater, L. E., Application of the DNDC model to tile-drained Illinois agroecosystems: model comparison of

conventional and diversified rotations. *Nutr. Cycl. Agroecosyst.* **2007**, DOI 10.1007/s10705-006-9074-2.

33. Xu-Ri; Wang, M.; Wang, Y. Using a modified DNDC model to estimate N2O fluxes from semi-arid grassland in China. *Soil Biol. Biochem.* **2003**, *35*, 615–620.
34. Li, C.; Salas, W.; DeAngelo, B.; Rose, S. Assessing Alternatives for Mitigating Net Greenhouse Gas Emissions and Increasing Yields from Rice Production in China Over the Next Twenty Years. *J. Environ. Qual.* **2006**, *35* (4), 1554–1565.
35. Giltrap, D.; Saggar, S.; Li, C.; Wilde, H. Using the NZ–DNDC model to estimate agricultural N2O emissions in the Manawatu–Wanganui region. *Plant Soil* **2008**, *309* (1), 191–209.
36. Pathak, H.; Li, C.; Wassmann, R. Greenhouse gas emissions from Indian rice fields: calibration and upscaling using the DNDC model. *Biogeosciences* **2005**, *2* (2), 113–123.
37. Butterbach-Bahl, K.; Kesik, M.; Miehle, P.; Papen, H.; Li, C. Quantifying the regional source strength of N-trace gases across agricultural and forest ecosystems with process based models. *Plant Soil* **2004**, *260*, 311–329.
38. Sleutel, S.; De Neve, S.; Beheydt, D.; Li, C.; Hofman, G. Regional simulation of long-term organic carbon stock changes in cropland soils using the DNDC model: 1. Large-scale model validation against a spatially explicit data set. *Soil Use Manage.* **2006**, *22* (4), 342–351.
39. Neufeldt, H.; Schafer, M.; Angenendt, E.; Li, C.; Kaltschmitt, M.; Zeddies, J. Disaggregated greenhouse gas emission inventories from agriculture via a coupled economic-ecosystem model. *Agric., Ecosyst. Environ.* **2006**, *112* (2-3), 233–240.
40. Brown, L.; Syed, B.; Jarvis, S. C.; Sneath, R. W.; Phillips, R. L.; Goulding, K. W. T.; Li, C. Development and application of a mechanistic model to estimate emission of nitrous oixde from UK agriculture. *Atmos. Environ.* **2002**, *36*, 917–928.
41. Seitzinger, S.; Harrison, J. A.; Böhlke, J. K.; Bouwman, A. F.; Lowrance, R.; Peterson, B.; Tobias, C.; Van Drecht, G. Denitrification across landscapes and waterscapes: a synthesis. *Ecol. Appl.* **2006**, *16*, 2064–2090.
42. Butterbach Bahl, K.; Gundersen, P.; Ambus, P.; Augustin, J.; Beier, C.; Boeckx, P.; Dannemann, M.; Gimeno, B. S.; Kiese, R.; Kitzler, B.; Ibrom, A.; Rees, R. M.; Smith, K. A.; Stevens, C.; Vesala, T.; Zechmeister-Boltenstern, S., Nitrogen processes in terrestrial ecosystems. In *European Nitrogen Assessment*; Sutton, M., Howard, C., Erisman, J. W., Billen, G., Bleeker, A., van Grinsven, H., Grennfelt, P., Grizzetti, B., Eds.; Cambridge University Press: Cambridge, U.K., 2011; pp 99−125.
43. Ciais, P.; Wattenbach, M.; Vuichard, N.; Smith, P.; Piao, S. L.; Don, A.; Luyssaert, S.; Janssens, I. A.; Bondeau, A.; Dechow, R.; Leip, A.; Smith, P.; Beer, C.; van der Werf, G. R.; Gervois, S.; Van Oost, K.; Tomelleri, E.; Freibauer, A.; Schulze, E. D. The European carbon balance. Part 2: croplands. *Glob. Change Biol.* **2010**, *16*, 1409–1428.

44. Skiba, U.; Smith, K. A. The control of nitrous oxide emissions from agricultural and natural soils. *Chemosphere: Global Change Sci.* **2000**, *2* (3-4), 379–386.
45. Erisman, J. W.; van Grinsven, H.; Leip, A.; Mosier, A.; Bleeker, A. Nitrogen and Biofuels; an overview of the current state of knowledge. *Nutr. Cycl. Agroecosyst.* **2010**, *86* (2), 211–223.
46. Halleux, H.; Lassaux, S.; Renzoni, R.; Germain, A. Comparative life cycle assessment of two biofuels ethanol from sugar beet and rapeseed methyl ester. *Int. J. Life Cycle Assess.* **2008**, *13* (3), 184–190.
47. Winiwarter, W. National Greenhouse Gas Inventories: Understanding Uncertainties versus Potential for Improving Reliability. *Water, Air, Soil Pollut.: Focus* **2007**, *7* (4), 443–450.
48. Leip, A. Quantitative quality assessment of the greenhous gas inventory for agriculture in Europe. *Clim. Change* **2010**, *103* (1-2), 245–261.
49. Del Grosso, S. J.; Ogle, S. M.; Parton, W. J.; Breidt, F. J. Estimating uncertainty in N_2O emissions from U.S. cropland soils. *Global Biogeochem. Cycles* **2010**, *24* (1), GB1009.
50. Sutton, M.; Billen, G.; Bleeker, A.; Erisman, J. W.; Grennfelt, P.; Van Grinsven, H.; Grizzetti, B.; Howard, C.; Leip, A. European Nitrogen Assessment - Technical Summary. In *European Nitrogen Assessment*; Sutton, M., Howard, C., Erisman, J. W., Billen, G., Bleeker, A., van Grinsven, H., Grennfelt, P., Grizzetti, B., Eds.; Cambridge University Press: Cambridge, U.K., 2011.
51. Millenium EcosystemsAssessment, *Ecosystems and human well-being*; Island Press: Washington, DC, 2005; Vol. 5.
52. Beringer, T. I. M.; Lucht, W.; Schaphoff, S. Bioenergy production potential of global biomass plantations under environmental and agricultural constraints. *GCB Bioenergy* **2011**.
53. Ainsworth, E. A.; Ort, D. R. How Do We Improve Crop Production in a Warming World? *Plant Physiol.* **2010**, *154* (2), 526.
54. Freibauer, A.; Kaltschmitt, M. Controls and models for estimating direct nitrous oxide emissions from temperate and sub-boreal agricultural mineral soils in Europe. *Biogeochemistry* **2003**, *63* (1), 93–115.
55. Beheydt, D.; Boeckx, P.; Sleutel, S.; Li, C.; Cleemput, O. v. Validation of DNDC for 22 long-term N_2O field emission measurements. *Atmos. Environ.* **2007**, *41*, 6196–6211.
56. Fumoto, T.; Kobayashi, K.; Li, C.; Yagi, K.; Hasegawa, T. Revising a process-based biogeochemistry model (DNDC) to simulate methane emission from rice paddy fields under various residue management and fertilizer regimes. *Glob. Change Biol.* **2008**, *14* (2), 382–402.
57. Butterbach-Bahl, K.; Kahl, M.; Mykhayliv, L.; Werner, C.; Kiese, R.; Li, C. A European wide inventory of soil NO emissions using the biogeochemical models DNDC/ Forest DNDC. *Atmos. Environ.* **2008**, *43* (7), 1392–1402.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

Chapter 20

Development of Spatial Inventory of Nitrous Oxide Emissions from Agricultural Land Uses in California Using Biogeochemical Modeling

Lei Guo,*,[1] Dongmin Luo,[1] Changsheng Li,[2] and Michael FitzGibbon[1]

[1]Research Division, California Air Resources Board,
Sacramento, California
[2]Institute for the Study of Earth, Oceans, and Space,
University of New Hampshire, Durham, New Hampshire
***E-mail: lguo@arb.ca.gov**

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) that contributes to global warming. In California, agricultural soil management is recognized as an important source of N_2O. It contributed over 50% of the total N_2O inventory in 2008. We evaluated N_2O emissions from agricultural soils in California using the biogeochemical model Denitrification-Decomposition (DNDC). Emission fluxes of N_2O from 17 types of agricultural land uses in 49 counties were simulated based on California-specific data of soil, land use, meteorology, and land management practices. The study indicated that N_2O fluxes varied tremendously across the landscape. Total annual N_2O emission derived directly from all agricultural soils statewide was about 1.27×10^4 ton N, with more than 83% from the Central Valley. Annual fluxes of N_2O ranged from 15.4 Kg N/ha from cotton fields to 0.03 Kg N/ha from rice paddies, with an average of 3.7 Kg N/ha from all agricultural land uses. Kings is the highest emitting county, which contributed approximately 17% of the total N_2O emissions from California's agricultural soils, followed by San Joaquin (11%), Fresno (11%), and Tulare (11%) counties. We provided emission maps displaying spatial distribution of N_2O emissions from agricultural soils that reflected local site-specific conditions. However, our emission estimates are subject to significant uncertainties with regard to

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

the input data, especially farming management parameters, and should not be viewed as real case emission scenarios. The study nevertheless demonstrates the usefulness of process-based geochemical modeling in assessing spatial distribution of N_2O emissions from agricultural soils. Extensive field studies are underway monitoring N_2O fluxes from major California cropping systems. The results from these studies will be used to improve our model and thus reduce the uncertainties of the emission estimates.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

Introduction

Nitrous oxide, or N_2O, is a naturally occurring gas with an estimated lifetime of 120 years in the atmosphere (*1*). With its broader absorption spectrum in the infrared range, N_2O is one of the most potent naturally occurring greenhouse gases (GHGs). The Intergovernmental Panel on Climate Change (IPCC) has determined its Global Warming Potential (GWP) to be 298 CO_2 equivalent (CO_2e) over 100-year time horizon, more than ten times that of the next significant contributing GHG methane (CH_4) which has a GWP of 25 (*2*).

N_2O is mainly produced from natural processes of nitrification, denitrification, and combustion. Nitrification and denitrification are common soil processes which play a vital role in nitrogen (N) cycling in ecosystems. However, agricultural activities involving intensive soil management, such as N fertilizer application and irrigation, can enhance nitrification and denitrification, causing elevated N_2O emissions that are far above the natural background. According to United States Environmental Protection Agency (USEPA), nitrification and denitrification are responsible for approximately 7.5×10^5 ton of N_2O produced in the United States in 2008, primarily from agricultural soils associated with crop production (*3*). In California, about 2.3×10^4 ton of N_2O was estimated to be emitted from agricultural soils in 2008, representing 54% of the total N_2O inventory in the State (*4*).

The conventional way of estimating N_2O emissions from agricultural soils is to use the emission factor (EF) approach, which assumes that a fixed fraction of the nitrogen applied to the soil is converted to N_2O. However, emission of N_2O from soil is a microbe-driven process, affected by numerous environmental factors that govern microbial activities. Fluxes of N_2O emissions are found to be related not only to N fertilizer application rate (*5–7*), but also to soil organic matter content (*8–10*), soil water content (*11–14*), soil pH (*7*, *15–17*), land cover (*6*, *18*, *19*), management practices (*20–23*), as well as meteorological conditions (*18*, *19*, *24–26*).

Due to both spatial and temporal variability of N_2O fluxes, it is extremely challenging to characterize N_2O emissions from agricultural soils quantitatively. Process-based biogeochemical models such as DAYCENT (*27–30*) and DNDC (*31–33*) have been developed to characterize the complicated interactions of biological, chemical, and physical processes in soil, and used to simulate emissions of trace gases produced from these interactions. USEPA has employed

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

a hybrid methodology combining both DAYCENT modeling and the IPCC emission factor approach in the development of national N_2O inventory from agricultural soils (*3*). The purpose of this study was to explore and demonstrate the use of the biogeochemical model DNDC as a methodology to estimate N_2O emissions from various cropping systems in California and to develop N_2O emission maps that reflect site specific crop, soil, weather, and agricultural land management conditions. DNDC has been applied and verified for many cropping systems worldwide (*34–37*). The model has also been used to assess carbon dynamics and sequestration potential of agricultural soils in California (*38*).

Methodology

DNDC Model

Denitrification-Decomposition, or DNDC, is a biogeochemical model formulated to simulate carbon (C) and N interactions and cycling in agricultural ecosystems (*31–33*). Built upon fundamental biogeochemical processes of decomposition, fermentation, nitrification, and denitrification, the DNDC model incorporates classic laws of physics, chemistry, and biology as well as many empirical equations developed from extensive scientific literatures. The model is capable of predicting dynamics of carbon and nitrogen species, including production of trace gases of CO_2, CH_4, N_2O, NO_X, and NH_3 in ecosystems, based on the basic ecological drivers of crop, soil, weather, and management activities (Figure 1). It consists of three submodels which simulate the mass transfer of heat and water (the thermal-hydraulic submodel), carbon species (the decomposition submodel), and nitrogen species (the denitrification submodel), respectively. DNDC can be used to analyze C and N cycling at the field, regional, or national scale depending on the spatial resolution of the input GIS database that specifies temporal and spatial variations of the basic ecological drivers.

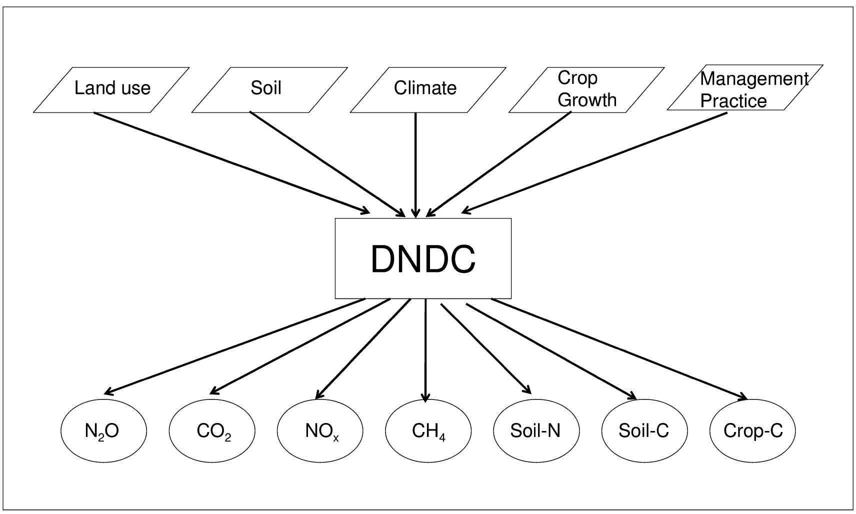


Figure 1. DNDC data requirements and outputs.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

Data Sources

Most of our data sources were from the public domain. The land use data was obtained from the Land Use Survey of the California Department of Water Resources (CDWR) (*39*) and the 2002 Census of Agriculture of the National Agricultural Statistics Service, the U.S. Department of Agriculture (USDA) (*40*). The CDWR's Land Use Survey data for the counties simulated in this study was collected between mid-1990s and 2006 and contains spatial information on agricultural, urban, and native vegetation lands, including description of land cover, acreage, and, when appropriate, irrigation method and water sources. The urban and native vegetation lands were eliminated, however, from the simulation because our study focused only on agricultural lands. The USDA's Census of Agriculture provides only agricultural land use data, aggregated at the county level. We simulated GHG emissions from 49 out of the 58 counties in California, covering an area of 3.4 x 10^6 ha, about 99% of the total harvested crop lands (referred to as "agricultural land uses" thereafter) in the State. The N_2O emissions were simulated using the data from the 2002 Census of Agriculture, but spatial distribution of the N_2O fluxes was allocated based on the CDWR's Land Use Survey data. Seventeen types of agricultural land uses were simulated as shown in Table 1. We did not model land uses at the subclass level of the CDWR's Land Use Survey, which tracked down specific crops. Instead, all crops were grouped into broad categories based on their phenological and physiological characteristics. For example, eggplants, peppers, cucumbers, and tomatoes, etc. were all grouped as vegetables. The tree crops were divided into either deciduous or evergreen orchards.

The soils data source was from the Soil Survey Geographic database (SSURGO) of the Natural Resources Conservation Service, USDA (*41*). SSURGO is a complicated soil survey database containing detailed soil distribution and profile information for the entire United States. Four soil properties were taken directly from SSURGO: soil organic carbon (SOC) content, soil density, soil pH, and soil clay fraction. We calculated the area-weighted means of the four soil properties of the top soil horizons for each county by overlying the polygons of soil components layer (COMP) from SSURGO in that county with those of the agricultural land uses from the Land Use Survey of the CDWR. These four soil parameters were then used as basic drivers to establish, based on the built-in empirical relations of the DNDC model, other soil characteristics, such as soil porosity, saturated hydraulic conductivity, field capacity, wilting point, and specific heat, required for the DNDC model.

The meteorological data was obtained from the California Weather Database (*42*) of the University of California (UC), Davis. The UC database stores current and historical weather data for approximately 400 weather stations throughout California. Daily precipitation, minimum and maximum temperatures, and solar radiation data are available from three network sources: (1) the California Irrigation Meteorological Information System (CIMIS) stations of the CDWR, (2) the National Oceanic and Atmospheric Administration (NOAA) stations of the United States Department of Commerce, and (3) the TouchTone (TT) stations of the UC TT Network. The data records of all networks were pooled to obtain a coverage as complete and uniform as possible in the simulated area. Missing records were filled by taking averages of nearby stations.

We used "typical" management practices in the simulation. The management practices were developed largely from the University of California Cooperative Extension (UCCE) reports; the Cost and Return Studies of the Department of Agricultural and Resource Economics, UC Davis; and personal communications with the UCCE staff. The irrigation practices were, however, simulated using the DNDC Irrigation Index 1, which sets soil water content automatically to field capacity to meet plant demands at 100%. The option of Irrigation Index 1 represents optimum irrigation conditions where no over-irrigation or water stress occurs. In reality, however, irrigation methods in California are extremely diversified, covering practices from broad furrow flooding to high precision micro-sprinklers or subsurface dripping. Irrigation records are one of the data sources that are especially difficult to obtain, or do not exist.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

Model Scenarios

Our model scenarios were developed to represent baseline N_2O emissions in 49 out of 58 California counties. Land uses in the nine remaining counties are either dominantly urban or native vegetation. The DNDC model was run using the meteorological data of 1990 to 2008 for each county. The model was first calibrated for each of the 17 major crop types to achieve a net carbon, nitrogen, and heat balance in and out of the cropping system while sustaining the expected yield and total biological mass produced. The final calibrated model thus represented the overall mass flow and plant growth well, although not validated against site-specific N_2O emission fluxes due to lack of monitoring data.

To simulate baseline N_2O emissions, we used "typical" management practices and "representative" soil parameter values. No alternative scenarios with regard to management activities were simulated that would produce different emission estimates of N_2O. Soil emissions with minimum and maximum soil parameter values for the four basic soil properties, i.e., soil organic carbon content, soil density, soil clay content, and pH, were also simulated for uncertainty analyses. These estimates would provide potential range of emission estimates due to variability of soil properties. Additional uncertainties associated with management practices such as irrigation and crop residue management were not explored in the study.

Four nitrogen sources were included in the modeling study: (1) N fertilizer application; (2) biological fixation of atmospheric N_2 in legume and, to a lesser extent, non-legume crops; (3) land application of livestock (primarily dairy) wastes; and (4) atmospheric deposition of nitrogen from precipitation. Application of livestock wastes or manure was only made in the eight counties where significant dairy operations exist: Fresno, Kern, Kings, Madera, Merced, San Joaquin, Stanislaus, and Tulare. About 28% of the total N generated from dairy manure in these counties was assumed to be applied to the following forage crops: corn, wheat, oats, sorghum, alfalfa, and non-legume hay *(R. Zhang, personal communication;* (*43*, *44*)*)*. The application of chemical nitrogen fertilizers in those crops was reduced accordingly to maintain the same nitrogen rates as in other counties without manure applications.

Results and Discussion

As shown in Figure 2, about 9% of California land, or 3.5 x 10^6 ha, is used actively for agricultural production, most of which is located in the Central Valley. Major agricultural counties include Fresno, Kern, Tulare, Kings, and San Joaquin in the San Joaquin Valley, and Glenn, Colusa, Yolo, Butte, and Sutter in the Sacramento Valley. According to the 2002 Census of Agriculture (*40*), major crops cultivated in California are orchards (1.2 x 10^6 ha), forage hay (7.9 x 10^5 ha), vegetables (4.8 x 10^5 ha), cotton (2.8 x 10^5 ha), and corn (2.3 x 10^5 ha).

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

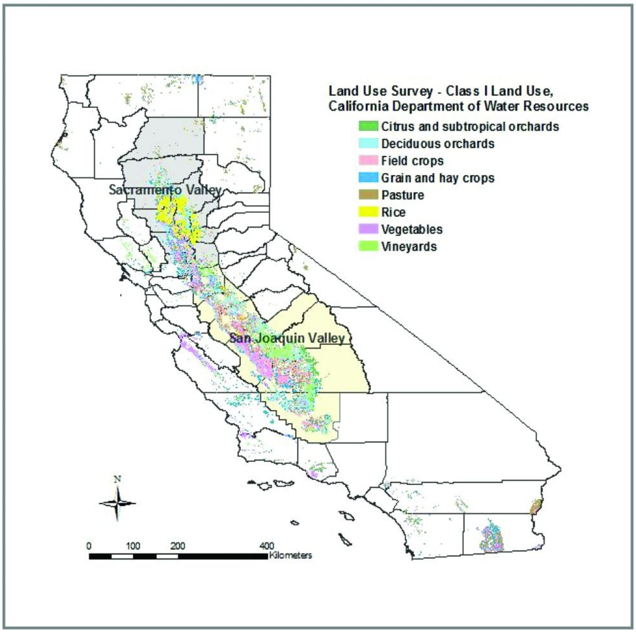

Land Use Survey - Class I Land Use,
California Department of Water Resources
🟩 Citrus and subtropical orchards
🟦 Deciduous orchards
🟪 Field crops
🟦 Grain and hay crops
🟫 Pasture
🟨 Rice
🟪 Vegetables
🟩 Vineyards
Sacramento Valley
San Joaquin Valley
N
0
100
200
400
Kilometers

Figure 2. Distribution of agricultural land uses in California. (Data source: Land Use Survey, California Department of Water Resources. Data retrieved March, 2009.) (see color insert)

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

Table 1. List of agricultural land uses, cultivation areas, and N fertilizer application rates simulated in the DNDC modeling.

	Area		*Fertilizer rate*
Crop	*ha*	*% total*	*Kg N/ha*
Alfalfa	444510	13.05	18
Barley	28903	0.85	45
Beans	22923	0.67	88
Corn	226290	6.64	255
Cotton	280242	8.23	280
Deciduous orchards	608689	17.87	112
Evergreen orchards	179228	5.26	123
Non-legume hay	333413	9.79	224
Oats	12801	0.38	67
Potato	21489	0.63	305
Rice	214726	6.30	135
Sorghum	4664	0.14	157
Sugarbeets	22373	0.66	210
Sunflower	6464	0.19	105
Vegetables	475130	13.95	184
Vineyards	359497	10.56	50
Wheat	164320	4.82	144
Total	3405662	100	

Table 2 lists the N_2O fluxes, emission factors (i.e., emission potentials), and total N_2O emissions for the 17 types of agricultural land uses simulated in this study. Although we ran the DNDC model using historical meteorological data, we used static land use data (most closely represented by year 2002), and constant crop management data in the simulation. As shown in Table 2, total statewide annual emission of N_2O derived directly from all agricultural land uses was estimated to be 1.27×10^4 ton N, equivalent to 6.17 million metric tons (mmt) CO_2e. Cotton and non-legume hay contributed almost 60% of the total N_2O emission, followed by alfalfa (14%), corn (10%), vegetables (9%), and deciduous orchards (3%). The least contributing crop was rice, whose emissions constituted < 0.05% of the total N_2O. The relative contribution of a particular land use to the total N_2O emission is dependent on both its emission fluxes and its cultivation area. For example, potato system generates high N_2O fluxes, but its contribution to the total N_2O emission in California was only <1% due to its limited acreage (Table 1).

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

Table 2. Annual N_2O fluxes, emission factors, and N_2O emissions for the 17 types of agricultural land uses simulated in California. Values are annual averages over 2000 to 2008.

	N_2O flux	*EF*	*Total N_2O*	
Crop	*Kg N/ha*	*Kg N/Kg N*	*ton, N*	*%total*
Alfalfa	4.07	0.226	1807.0	14.28
Barley	0.26	0.006	7.6	0.06
Beans	0.93	0.011	21.3	0.17
Corn	5.31	0.021	1202.5	9.50
Cotton	15.37	0.055	4306.0	34.02
Deciduous orchards	0.52	0.005	318.3	2.51
Evergreen orchards	0.12	0.001	21.1	0.17
Non-legume hay	9.74	0.043	3248.2	25.66
Oats	0.70	0.010	8.9	0.07
Potato	3.99	0.013	85.8	0.68
Rice	0.03	0.0002	6.5	0.05
Sorghum	2.27	0.014	10.6	0.08
Sugarbeets	0.56	0.003	12.5	0.10
Sunflower	1.85	0.018	12.0	0.09
Vegetables	2.43	0.013	1156.9	9.14
Vineyards	0.62	0.012	221.4	1.75
Wheat	1.28	0.009	210.8	1.67
Mean /Overall	3.72[a]	0.022[b]		
Total			12657.5	100.0

[a] Area-weighted mean. [b] Value derived from correlation analysis (see Figure 3).

The fact that N_2O emission fluxes varied tremendously across different crop lands demonstrates the extremely variable nature of N_2O production from agricultural soils. Although many factors can contribute to this variability, the effect of N fertilizer application rate is well recognized and is the basis for the IPCC Tier 1 Emission Factor approach (*45*). Figure 3 shows the correlation of the simulated N_2O emission fluxes for the 17 types of agricultural land uses with their N application rates, including both chemical fertilizers and livestock manure. Although the relationship for individual crops is scattered, an overall correlation between N_2O flux (Y) and the N fertilizer application rate (X) can be derived as $Y = 0.022X$ at the significance level of < 0.01, where the slope of 0.022 is the overall EF.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

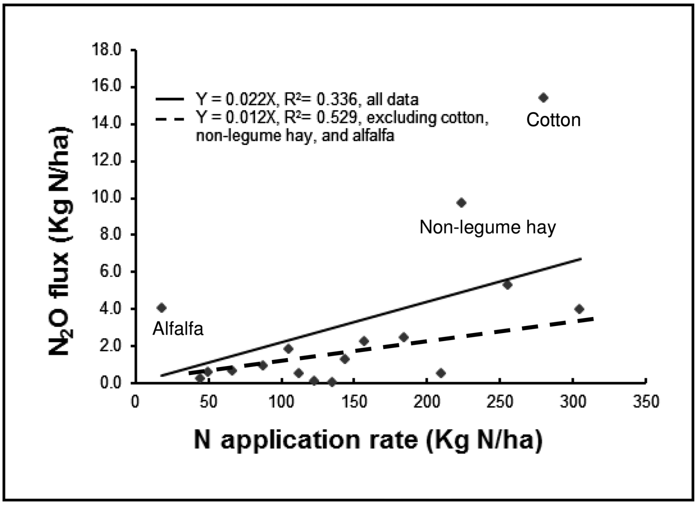


Figure 3. Correlation of N_2O fluxes with nitrogen application rates for the 17 types of agricultural land uses in California simulated in the DNDC modeling.

Alfalfa was identified to have the highest EF (EF = 0.226), followed by cotton (0.055), non-legume hay (0.044), and corn (0.021). The unusually high EF for alfalfa was due to its strong capacity of biological fixation for atmospheric N_2, which could provide an additional annual rate of over 300 kg N/ha in California conditions. Given the particularly low N fertilizer application rate of alfalfa (18 Kg N/ha, Table 1), this high EF, when applied to the low N application rate, would not lead to strong N_2O fluxes from alfalfa fields. The average N_2O flux for alfalfa is calculated to be 4.07 Kg N/ha, ranking behind cotton, non-legume hay, and corn (Table 2). The non-legume hay can also fix small amounts of N from the atmosphere (15–20 Kg N/ha), which would also inflate its EF slightly.

The high EF for cotton is probably related to its relatively higher crop residue in the field (90%) compared to most other crops such as alfalfa, non-legume hay, and fruit trees. The lowest EF (0.0002) was calculated for rice, due to presumably the prolonged flooded condition that depleted soil oxygen required for nitrification, a critical step for N_2O formation in soil. Therefore, the overall EF could significantly over- or under-estimate N_2O emissions of an individual crop. Without considering the three highest emitting crops of cotton, non-legume hay, and alfalfa, the overall EF would decrease to 0.012, which is close to that of the IPCC default EF of 0.01 for direct emissions (*45*) (Figure 3.).

As our model does not include indirect emissions caused by offsite movement of N species by leaching, runoff, and volatilization, the direct EFs presented in Table 2 only represent part of the N_2O emission potentials from the cropping systems. Indirect emissions can also contribute significant amount of N_2O and some cropping systems may have higher indirect emissions than others depending on the management practices. Future research is needed to provide more quantitative assessment of indirect emissions from different cropping systems. Although the direct EF for rice is low, it is not clear, for example, how much indirect emissions of N_2O would occur when the rice water was released to drainage channels and further carried away into surface water systems.

N_2O Emissions by County

Total N_2O emissions and ranking of individual counties are shown in Figure 4. Kings was the highest emitting county; its emissions alone accounted for 17% of the total emission of N_2O in California from all agricultural lands. San Joaquin, Fresno, and Tulare each contributed about 11%, followed by Merced (8%), Kern (7%), and Stanislaus (5%). Most of the N_2O emissions came from the San Joaquin Valley, i.e. the southern part of the Central Valley (Figure 2). Sacramento County, with its contribution of 4%, was the largest emitting county in the Sacramento Valley.

Land use patterns in the San Joaquin Valley differ markedly from those in the Sacramento Valley. Fertilizer-intensive land uses, such as cotton and corn, are prevalently more abundant in the top emitting counties in the San Joaquin Valley than the low emitting counties in the Sacramento Valley. The amount of N fertilizer received in a county, however, does not necessarily reflect N_2O emissions of the county. We developed an emission map of N_2O for the counties based solely on the modeled N application rates using the IPCC default direct emission factor of 0.01 (Figure 5). A comparison of this map with that developed by the DNDC model (Figure 4) reveals marked discrepancy, although both maps show the Central Valley to be the leading areal source of N_2O. The simple EF method which ignored any site specific information on land use, soil, weather, and management practices other than N fertilizer application would over predict N_2O emissions for Sutter, Butte, and Yuba counties in the Sacramento Valley, but under predict emissions for Kings, Tulare, San Joaquin, and Fresno counties in the San Joaquin Valley. The overestimation was most pronounced for counties with predominantly rice paddies, where emission fluxes of N_2O could be overestimated by a factor of 3. Most of the underestimation happened for counties with larger acreages of cotton, non-legume hay, and alfalfa in the San Joaquin Valley, since these land uses have EF values (0.044 to 0.226) which are far above that that of the overall EF (0.022). It must be noted that the DNDC-derived EF cannot be compared directly with the IPCC default EF because the former includes all N inputs into the ecosystems, including biological fixation of atmospheric N_2 from legume and non-legume crops.

Spatial Variability of N_2O Emissions

As expected, N_2O fluxes varied tremendously across landscape due to variation in environmental factors that influence soil microbial activities and N availability. We developed maps of N_2O emissions for all agricultural land uses in each of the 49 counties simulated. As an illustration, Figure 6 shows the average annual N_2O fluxes simulated for Sacramento and Fresno Counties. Since some of the land use data that we used may be out of date, these maps should be viewed only as a snapshot of the spatial variation of N_2O emissions in California. Tremendous efforts would be required to improve the spatial resolution and

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

accuracy of the GIS database used for parameterizing the DNDC model in order to reduce the uncertainties with these maps.

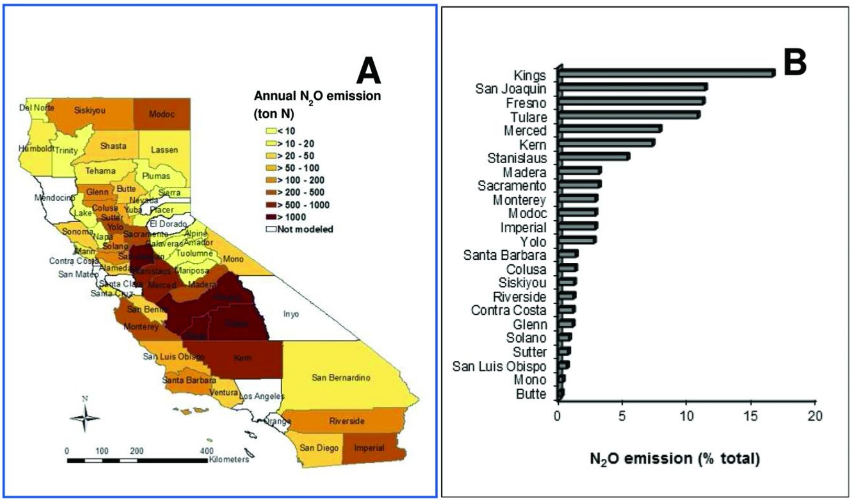

A
Annual N_2O emission (ton N)
< 10
> 10 - 20
> 20 - 50
> 50 - 100
> 100 - 200
> 200 - 500
> 500 - 1000
> 1000
Not modeled
Del Norte
Siskiyou
Modoc
Humboldt
Trinity
Shasta
Lassen
Tehama
Plumas
Glenn
Butte
Sierra
Mendocino
Lake
Colusa
Yuba
Nevada
Placer
Sutter
Yolo
El Dorado
Sonoma
Napa
Sacramento
Alpine
Solano
Calaveras
Amador
Marin
Tuolumne
Contra Costa
San Joaquin
Mono
San Mateo
Alameda
Stanislaus
Mariposa
Santa Clara
Merced
Madera
Santa Cruz
Fresno
Inyo
San Benito
Tulare
Monterey
Kings
San Luis Obispo
Kern
Santa Barbara
San Bernardino
Ventura
Los Angeles
Orange
Riverside
San Diego
Imperial
N
0
100
200
400
Kilometers
B
Kings
San Joaquin
Fresno
Tulare
Merced
Kern
Stanislaus
Madera
Sacramento
Monterey
Modoc
Imperial
Yolo
Santa Barbara
Colusa
Siskiyou
Riverside
Contra Costa
Glenn
Solano
Sutter
San Luis Obispo
Mono
Butte
0
5
10
15
20
N_2O emission (% total)

Figure 4. DNDC simulated regional distribution of annual N_2O emissions (A) and ranking (B) for California counties. Values are annual averages over 2000 to 2008. (see color insert)

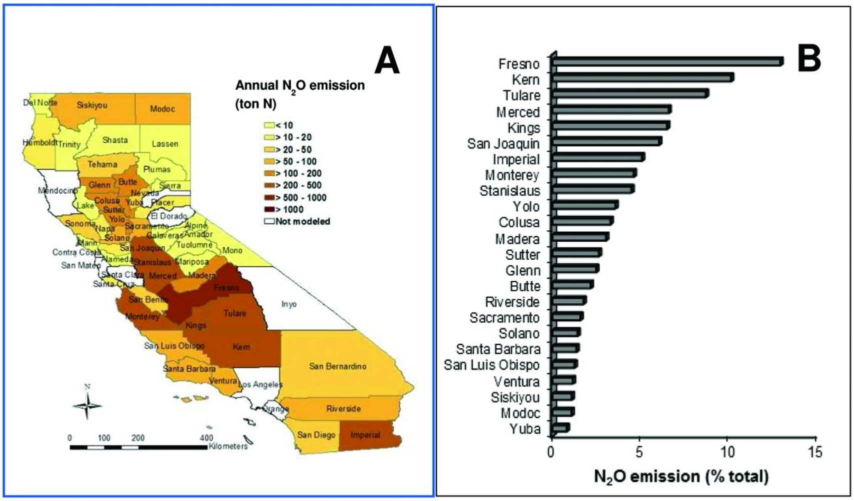

A
Annual N_2O emission (ton N)
< 10
> 10 - 20
> 20 - 50
> 50 - 100
> 100 - 200
> 200 - 500
> 500 - 1000
> 1000
Not modeled
Del Norte
Siskiyou
Modoc
Humboldt
Trinity
Shasta
Lassen
Tehama
Plumas
Glenn
Butte
Sierra
Mendocino
Lake
Colusa
Yuba
Nevada
Placer
Sutter
Yolo
El Dorado
Sonoma
Napa
Sacramento
Alpine
Solano
Calaveras
Amador
Marin
Tuolumne
Contra Costa
San Joaquin
Mono
San Mateo
Alameda
Stanislaus
Mariposa
Santa Clara
Merced
Madera
Santa Cruz
Fresno
Inyo
San Benito
Tulare
Monterey
Kings
San Luis Obispo
Kern
Santa Barbara
San Bernardino
Ventura
Los Angeles
Orange
Riverside
San Diego
Imperial
N
0
100
200
400
Kilometers
B
Fresno
Kern
Tulare
Merced
Kings
San Joaquin
Imperial
Monterey
Stanislaus
Yolo
Colusa
Madera
Sutter
Glenn
Butte
Riverside
Sacramento
Solano
Santa Barbara
San Luis Obispo
Ventura
Siskiyou
Modoc
Yuba
0
5
10
15
N_2O emission (% total)

Figure 5. Calculated regional distribution of annual N_2O emissions (A) and ranking (B) for California counties based on the modeled nitrogen application rates and the IPCC direct emission factor of 0.01. (see color insert)

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

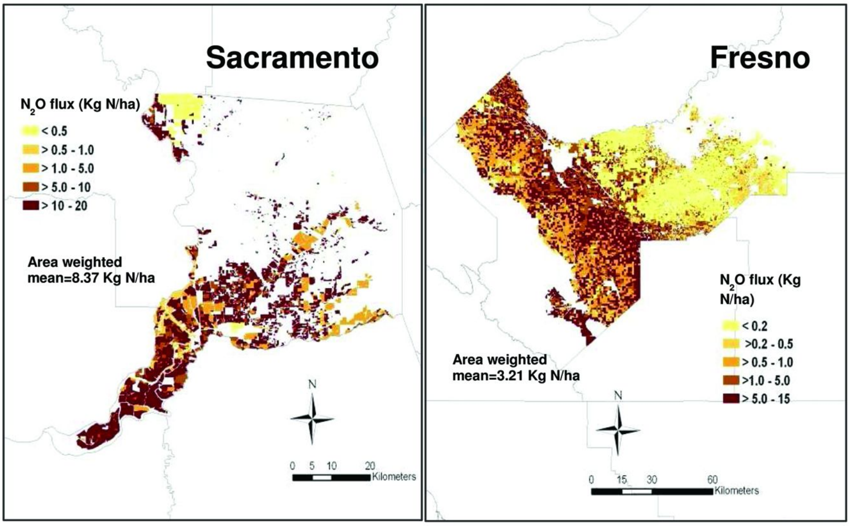


Figure 6. Spatial distribution of annual N_2O fluxes from agricultural land uses in Sacramento and Fresno counties. (see color insert)

An examination of all N_2O emission maps indicates that the highest emission spots of N_2O in California were cotton fields in Kings County, which had an annual flux of 26.9 Kg N/ha, while the lowest flux came from rice fields in Colusa County, which had an annual flux of 0.022 Kg N/ha. The average annual flux of N_2O for all agricultural land uses in California was 3.72 Kg N /ha. For a given crop, N_2O flux can vary by an order of magnitude depending on its geographic location. Figure 7 shows a comparison of N_2O fluxes from corn fields simulated for different counties by the DNDC model and that estimated by the IPCC EF method. The average annual flux of N_2O for a corn field in Sacramento County was 10.3 kg N/ha, but was only 2.7 Kg N/ha in Fresno County despite the fact that the latter received additional supply of organic carbon from livestock manure, which could increase SOC, an important soil characteristic conducive to N_2O emissions (*8–10*, *20*, *46*). Apparently, the climatic condition of higher temperature and lower precipitation in the San Joaquin Valley has impeded the building-up of SOC. The area-weighted mean SOC in Sacramento County was 3.7%, which is more than 7 times that of 0.5% in Fresno County. The average annual flux of N_2O from corn fields for all counties was 5.31 Kg N/ha, which is more than twice that estimated with the IPCC EF method (2.55 Kg N/ha). These results demonstrate that the mean EFs calculated for individual land uses, such as those presented in Table 2, should not be used as the simple indicator of their N_2O emission potentials. For a given land use, the emission potential can vary so much from one location to another that the variation can sometimes exceed its difference from other crops. Thus it is extremely important to take into consideration all factors of soil, crop, meteorology, and management practices when evaluating N_2O emissions from agricultural soils.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

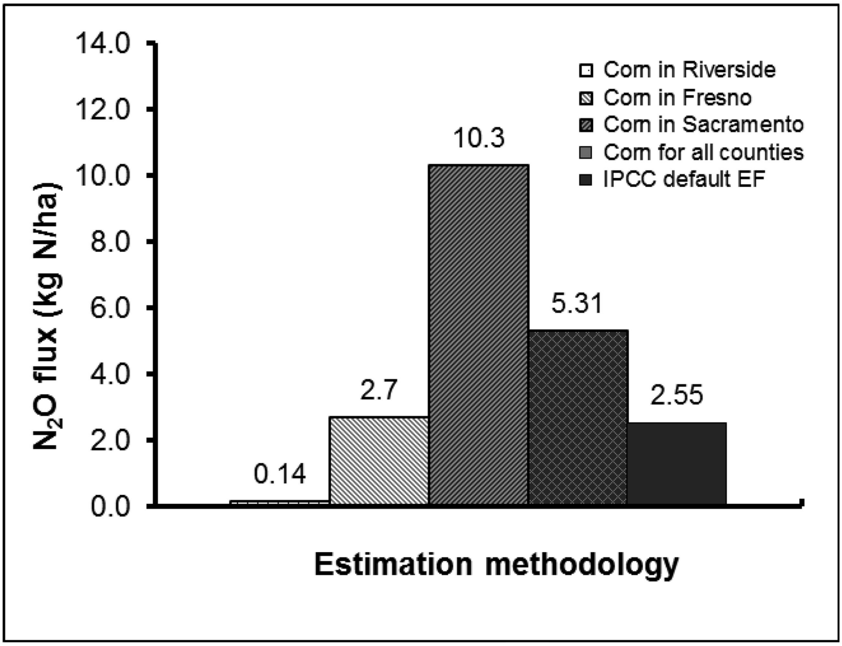


Figure 7. Comparison of estimated N_2O fluxes from corn fields from different California counties using DNDC modeling and by the IPCC direct emission factor of 0.01.

Uncertainties and Limitations

We assessed uncertainties in the DNDC model estimation using the Most Sensitive Factor (MSF) approach, in which effects of SOC on N_2O emissions were evaluated. The reliability of this approach has been discussed in detail in Li et al. (*32*, *47*). Of the four basic soil drivers used for the DNDC model, SOC is considered the most important one related to N_2O emissions (*20*, *46*, *47*). We used the minimum and maximum SOC values reported in the SSURGO soil database in the DNDC simulation to bracket the likely outcomes of N_2O emissions as a result of soil property variability. Based on this analysis, total annual N_2O emissions from agricultural soil management in California could range from 9.51 x 10^3 to 1.59 x 10^4 ton N, with the most likely value being 1.27 x 10^4 ton N, which was calculated using the representative SOC. We did not perform sensitivity analysis of variability associated with management practices such as fertilizer application rate, irrigation, tillage, or crop residual management in this exploratory study, which would definitely result in greater uncertainties for the emission estimates.

Our DNDC model was only calibrated for general C and N balances of the cropping systems under standard management practices. California specific N_2O emission data is urgently needed, especially from the high emitting crop sites of cotton and corn, to further refine the DNDC model. An extensive research program is currently underway in California to monitor N_2O fluxes from a variety

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

of California cropping systems. These studies will be used to further calibrate and validate the emission model developed in this study. It is expected that these efforts will significantly improve the model representation of the real world cases and reduce the uncertainties of the emission estimates.

Conclusions

DNDC modeling using California specific data of land use, soil, weather, and crop management practices indicated substantial variation of N_2O fluxes by land use and geographic location. Annual direct emissions of N_2O from agricultural land uses in California was estimated as 1.27 x 10^4 ton N. Average annual flux of all agricultural lands was 3.72 Kg N/ha, but varied from 15.4 Kg N/ha for cotton to 0.03 Kg N/ha for rice. The highest contributing counties were Kings, San Joaquin, Fresno, and Tulare, all from the San Joaquin Valley.

This study was based on “typical” management practices and ideal irrigation scenarios which may not represent accurately the real world cases and our land use data may be out of date. Therefore, our results should not be taken literally as the real case emission scenarios. They only show how process-based biogeochemical modeling can make use of the vast amount of data and best science available to produce information on diverse aspects of the GHG inventory with respect to agricultural soil management. This modeling study represents only a small step in that direction. With the ongoing and future research efforts, our model will be improved over time and provide more a reliable assessment of N_2O from agricultural soils.

Acknowledgments

The authors would like to express our sincere thanks to the following persons who have provided crop management information for the project: Dr. Karen M. Klonsky, Mr. Richard L. De Moura, Dr. Oleg Daugovish, Mr. Etaferahu Takele, Mr. Doug Munier, Dr. G. Stuart Pettygrove, Dr. Ruihong Zhang, and Ms. Priyashiela Singh of the University of California, Davis; Dr. Bruce McCarl of Texas A&M University; and Dr. William Salas of Applied Geosolutions, LLC. We also would like to thank Dr. Linying Li and Dr. Marc Vayssieres of the California Air Resources Board for their technical assistance and enlightening discussions over the course of this project.

Disclaimer

The statements and conclusions in this chapter are those of the authors and are not to be construed as an official endorsement or approval by the California Air Resources Board.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

References

1. Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2006; pp 35−36.
2. Intergovernmental Panel on Climate Change (IPCC); *Climate Change 2007: The Physical Science Basis;* Solomon, S., Qin D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press: Cambridge, United Kingdom, 2007.
3. United States Environmental Protecton Agency (USEPA); *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2008*, U.S. EPA # 430-R-10-006; Washington DC, 2010, URL http://www.epa.gov/climatechange/emissions/usinventoryreport.html.
4. California Air Resources Board; *Greenhouse Gas Inventory Data: 2000 to 2008*; 2010, URL http://www.arb.ca.gov/cc/inventory/data/data.htm.
5. Eichner, E. *J. Environ. Qual.* **1990**, *19*, 272–280.
6. Bouwman, A. F.; Boumans, L. J.; Batjes, N. H. *Global Biogeochem. Cycles* **2002**, *16*, 1058–1070.
7. Stehfest, E.; Bouwman, L. *Nutr. Cycling Agroecosyst.* **2006**, *74*, 207–228.
8. Bremner, J. M.; Breitenbeck, G. A.; Blackmer, A. M. *Geophys. Res. Lett.* **1981**, *8*, 353–356.
9. Khalil, M. I.; Rosenani, A. B.; Van Cleemput, O.; Fauziah, C. I.; Shamshuddin, J. *J. Environ. Qual.* **2002**, *31*, 1071–1078.
10. Halvorson, A. D.; Nielsen, D. C.; Reule, C. A. *Agron. J.* **2004**, *96*, 1196–1201.
11. Smith, K. A.; Ball, T.; Conen, F.; Dobbie, K. E.; Massheder, J.; Rey, A. *J. Soil Sci.* **2003**, *54*, 779–791.
12. Dobbie, K. E.; Smith, K. A. *Global Change Biol.* **2003**, *9*, 204–218.
13. Burger, M.; Jackson, L. E.; Lundquist, E. J.; Louie, D. T.; Miller, R. L.; Rolston, D. E.; Scow, K. M. *Biol. Fert. Soils* **2005**, *42*, 109–118.
14. Adviento-Borbe, M. A. A.; Doran, J. W.; Drijber, R. A.; Dobermann, A. *J. Environ. Qual.* **2006**, *35*, 1999–2010.
15. Ryden, J. C.; Lund, L. J. *Soil Sci. Soc. Am. J.* **1980**, *44*, 505–511.
16. Cheng, W.; Tsuruta, H.; Chen, G.; Yagi, K. *Soil Biol. Biochem.* **2004**, *36*, 953–963.
17. Morkved, P.; Dorsch, P.; Bakken, L. *Soil Boil. Biochem.* **2007**, *39*, 2048–2057.
18. Kaiser, E.-A.; Hohrs, K.; Kücke, M.; Schnug, E.; Heinemeyer, O.; Munch, J. C. *Soil Biol. Biochem.* **1998**, *30*, 1553–1563.
19. Dobbie, K. E.; McTaggart, I. P.; Smith, K. A. *J. Geophys. Res., [Atmos.]* **1999**, *104*, 26891–26899.
20. Flessa, H.; Dörsch, P.; Beese, F. *J. Geophys. Res.* **1995**, *100*, 23115–23123.
21. Venterea, R. T.; Stanenas, A. J. *J. Environ. Qual.* **2008**, *37*, 1360–1367.
22. Halvorson, A. D.; Del Grosso, S. J.; Alluvione, F. *J. Environ. Qual.* **2010**, *39*, 1554–1562.
23. Halvorson, A. D.; Del Grosso, S. J.; Alluvione, F. *Soil Sci. Soc. Am. J.* **2010**, *74*, 436–445.

24. Goodroad, L. L.; Keeney, D. R. *Can. J. Soil Sci.* **1984**, *64*, 187–194.
25. Flessa, H.; Beese, F. *Soil Sci. Soc. Am. J.* **1995**, *59*, 1044–1051.
26. Lee, J.; Hopmans, J. W.; van Kessel, C.; King, A. P.; Evatt, K. J.; Louie, D.; Rolston, D. E.; Six, J. *Agric. Ecosyst. Environ.* **2009**, *129*, 378–390.
27. Parton, W. J.; Hartman, M. D.; Ojima, D. S.; Schimel, D. S. *Global Planet. Change* **1998**, *19*, 35–48.
28. Del Grosso, S. J.; Parton, W. J.; Mosier, A. R.; Hartman, M. D.; Brenner, J.; Ojima, D. S.; Schimel, D. S. In *Modeling Carbon and Nitrogen Dynamics for Soil Management*; Schaffer, M., Ma, L., Hansen, S., Eds.; CRC Press: Boca Raton, Florida, 2001; pp 303−332.
29. Del Grosso, S. J.; Ojima, D. S.; Parton, W. J.; Mosier, A. R.; Peterson, G. A.; Schimel, D. S. *Environ. Pollut.* **2002**, *116*, S75–S83.
30. Del Grosso, S. J.; Mosier, A. R.; Parton, W. J.; Ojima, D. S. *Soil Till Res.* **2005**, *83*, 9–24.
31. Li, C.; Frolking, S.; Frolking, T. A. *J. Geophys. Res.* **1992**, *97*, 9759–9776.
32. Li, C.; Narayanan, V.; Harriss, R. C. *Global Biogeochem. Cycles* **1996**, *10*, 297–306.
33. Li, C. *Nutr. Cycling Agroecosys.* **2000**, *58*, 259–276.
34. Brown, L.; Syedb, B.; Jarvisa, S. C.; Sneathc, R. W.; Phillipsc, V. R.; Gouldingd, K. W. T.; Li, C. *Atmos. Environ.* **2002**, *36*, 917–928.
35. Cai, Z.; Sawamoto, T.; Li, C.; Kang, G.; Boonjawat, J.; Mosier, A.; Wassmann, R.; Tsuruta, H. *Global Biogeochem. Cycles.* **2003**, *17*, 1107–1116.
36. Babu, Y. J.; Li, C.; Frolking, S.; Nayak, D. R.; Adhya, T. K. *Nutr. Cycling Agroecosys.* **2006**, *74*, 157–174.
37. Smith, W. N.; Grant, B. B.; Desjardins, B. B.; Worth, D.; Li, C.; Boles, S. H.; Huffman, E. C. *Agric. Ecosyst. Environ.* **2010**, *136*, 301–309.
38. Li, C.; Salas, W.; Huertos, M. C. *Quantifying Carbon Dynamics and Greenhouse Gas Emissions in Agricultural Soils of California: A Scoping Study*; Publication Number: 500-04-038; California Energy Commission: Sacramento, California, 2004.
39. California Department of Water Resources (CDWR), Land Use Survey, URL http://www.water.ca.gov/landwateruse/lusrvymain.cfm.
40. United States Department of Agriculture (USDA), National Agricultural Statistics Service (NASS), 2002 Census of Agriculture, Washington DC, USA, URL http://www.agcensus.usda.gov/Publications/2002/index.asp.
41. United States Department of Agriculture (USDA), Natural Resources Conservation Service (NRCS), Soil Survey Geographic (SSURGO) Database, URL http://soils.usda.gov/survey/geography/ssurgo/.
42. University of California Statewide Intergrated Pest Management, Weather Data and Products, URL http://www.ipm.ucdavis.edu/WEATHER/wxretrieve.html.
43. Pettygrove, G. S.; Putnam, D. H.; Meyer, D. M. *Integrating Forage Production with Dairy Manure Management in the San Joaquin Valley*, University of California Agriculture Research and Education Program; University of California: Davis, California, 2003.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

44. Chang, A.; Letey, J.; Meyer, D.; Meyer, R. D.; Mathews, M. C.; Mitloehner, F.; Pettygrove, S.; Robinson, P.; Zhang, R. *Managing Dairy Manure in the Central Valley of California. Committee of Experts on Dairy Manure Management;* University of California: Riverside, California, 2005.
45. Intergovernmental Panel on Climate Change (IPCC); *2006 IPCC Guidelines for National Greenhouse Gas Inventories*; Eggleston, S., Buendia, L., Miwa, K., Ngara, T., Tanabe K., Eds.; Institute for Global Environmental Strategies (IGES): Hayama, Japan, 2006; Vol. 4.
46. Bouwman, A. F.; Boumans, L. J. M.; Batjes, N. H. *Global Biogeochem. Cycles* **2002**, *16*, 464–472.
47. Li, C.; Zhuang, Y.; Frolking, S.; Galloway, J.; Harriss, R.; Moore, B.; Schimel, S.; Wang, X. *Ecol. Appl.* **2003**, *13*, 327–336.

Downloaded by DUKE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch020

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

Chapter 21

Greenhouse Gas Emission Sources from Beef and Dairy Production Systems in the United States

Kimberly R. Stackhouse, Sara E. Place, Michelle S. Calvo, Qian Wang, and Frank M. Mitloehner*

Department of Animal Science, University of California, Davis,
2151 Meyer Hall, One Shields Avenue, Davis, CA 95616
***E-mail: fmmitloehner@ucdavis.edu**

Contribution of beef and dairy cattle production in the United States (U.S.) to anthropogenic climate change is a growing public policy concern. In recent years, research in this area has begun to quantify greenhouse gas (GHG) emission sources from beef and dairy cattle production systems and develop initial mitigation strategies to reduce GHG emissions without compromising animal productivity. Developing an in-depth and accurate understanding of GHG emission sources from these cattle systems is challenging because of the variability across farms, ranches, and feedlots, and the variation between animal types on individual operations. Emission sources can be distinguished into two main categories: enteric fermentation and manure. However, to fully quantify all GHG emission sources from the beef and dairy production systems, a Life Cycle Assessment (LCA) should be completed that includes all emission sources from cradle to fork. Included in this assessment would be GHG sources associated with animal management, emissions during processing, and emissions associated with transportation of the finished product to the consumer. This chapter focuses on GHG emissions from the dairy and beef production systems derived from enteric fermentation and manure.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

Introduction

Cattle production is considered an important anthropogenic source of greenhouse gases (GHG) contributing to climate change and has received considerable political and public attention in recent years. Two kinds of GHG emission sources have been identified from cattle production systems: direct and indirect emissions. Direct emissions refer to gases produced by the animal, including enteric fermentation and that are emitted from excreted feces and urine (*1*). Indirect emissions refer to gases that occur during the production of feed, including manure soil application, carbon dioxide (CO_2) during the production of fertilizer and other inputs used to grow feed crops, CO_2 from energy consumption during feed crop harvesting, and CO_2 from transportation of cattle, meat, and milk. Indirect and direct emissions are interlinked and dependent on the efficiency of the cattle production system and the length of the animal's productive life. Therefore, reporting emissions 'per unit of productive output' (e.g., kg of carcass weight for beef cattle and kg of milk for dairy cattle) rather than 'per head' allows for the proper accounting of emissions and development of the most effective mitigation techniques.

Developing an in-depth and accurate understanding of both the direct and indirect GHG emission sources from a whole system such as the dairy or beef industry requires a complete GHG Life Cycle Assessment (LCA). A LCA provides a comprehensive analysis of the GHG emission sources from the entire production system as supported with data from field monitoring. A LCA of the beef and dairy production systems includes all GHG emission sources from 'cradle to fork', which includes GHG from the entire supply chain. This in-depth analysis is beyond the scope of this chapter, and such an analysis has yet to be extensively evaluated due to the lack of comprehensive information that fully account for all GHG sources and potential sinks from beef and dairy production systems. Therefore, this chapter will focus primarily on direct GHG emission sources from dairy and beef cattle production.

Overview of the U.S. Beef and Dairy Industries

In 2009, the U.S. beef and dairy industries supplied 11.8 billion kg of beef and 85.9 billion kg of milk to human consumption (*2*). In 2010, there were a total of 100.8 million cattle, with approximately 90 million beef cattle (Continental and British Beef Breeds) and 10 million dairy cattle (predominantly Holstein and Jersey breeds) (*3*). The cattle industries span the continental U.S. and range from large to small scale operations. This makes the industries diverse and complex, and GHG emissions difficult to quantify.

In general, management of the beef industry is more extensive and more segmented than the dairy industry, which increases the variability of environmental emissions, such as GHGs. U.S. beef cattle production is most often comprised of a three-phase system with specialized producers in each sector: 1) cow-calf production, 2) stocker cattle production, and 3) finishing cattle production. In the cow-calf sector, cows are maintained extensively on pasture or rangeland and give birth to calves, which are weaned and sold at 6-8 months of age. In the

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

stocker sector, additional body weight is added to the weaned calf by grazing pasture and rangeland. The calf exits the stocker system at approximately 350 kg at 9-14 months of age. In both the cow-calf and stocker sectors, the majority of the pasture and rangeland used for grazing is not usable for row-crop production (e.g., corn, vegetables, soybean, etc.). The most intensive sector in beef cattle production is the finishing phase. This is the final phase and involves housing animals in a confined feedlot, where animals are fed a corn-rich concentrate diet to a harvest weight of approximately 550 kg at 14-20 months of age. In the feedlots, manure is managed and is typically removed from the pens every 4-6 months. This differs from pastures, where manure is un-managed and deposited directly on rangeland and pasture.

Unlike the three-phased beef cattle operations, dairy operations are more typically integrated on a single farm that houses calves, growing heifers, lactating cows, and dry cows. Animals are typically fed and maintained in confinement and manure is removed from housing areas on a daily basis. Typical manure management involves scraping corrals and piling into dry storage piles and/or scraping or flushing of manure from concrete floored freestall barns into liquid storage. Calves are fed a milk or milk replacer and grain supplement and are housed individually in calf hutches from birth until weaning (approximately 2 months of age). Growing heifers are housed in groups, fed a forage based total mixed ration (TMR), and are managed to calve at 2 years of age. Between lactation periods, dry cows (cows not lactating) are fed a high forage TMR for a 60 day period, which allows them to recuperate for the next lactation cycle. Lactating cows have high nutrient requirements; therefore, a properly balanced TMR is provided to reach maximum milk production levels. While many dairy operations still manage every aspect of production (from calf raising to lactation), there is a growing number of producers that specialize in producing heifers and young calves, especially for dairies with large herd sizes.

Manure management is an important component of large and small confined animal feeding operations in the U.S.. Manure that is managed properly can be a valuable resource for producers, because it contains nutrients that can be utilized for crop fertilization and to enhance soil quality (*4*). As facility size, herd size, and industry type (dairy versus beef, for instance) vary so will manure management strategies and manure holding structures that contain waste (animal manure, wastewater, contaminated runoff, and mixtures of manure with bedding (*5*)). Manure storage structures can comprise of areas or portions of buildings designated specifically for manure storage or treatment, whereas more sophisticated manure storage structures can consist of lagoons, pits, ponds, or tanks (*5*). After storage and treatment, manure and wastewater can be applied to pasture or crop fields as fertilizer. In addition, manure can also be managed using anaerobic digester systems or aerobic composting, to potentially reduce environmental impact, control odors, and capture biogas to be used as a source of energy (*6*).

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

Greenhouse Gas Emissions Sources from Beef and Dairy Production Systems

The three main GHG known to emanate from beef and dairy production are methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2). These gases are predominately emitted from enteric fermentation, animal respiration, and through microbial decomposition of manure. The following sections will detail the processes responsible for the production of these gasses.

Methane

Methane is the most well understood source of GHGs from beef and dairy production, as it was originally studied in significant depth to improve the nutritional use of feedstuffs in the rumen environment. Methane from cattle production is considered to be the most important source of anthropogenic CH4 emissions (*7*). Many factors affect CH_4 emissions from cattle including feed intake, animal size, diet, growth rate, milk production, and energy consumption (*1*, *8*). In beef and dairy production systems, methane is primarily produced from the microbial digestive processes of ruminant livestock species. This microbial fermentation is referred to as enteric fermentation, whereby CH_4 is produced as a by-product and expelled through eructation (*1*, *7*, *9*). As a ruminant, the bovine promotes digestion of cellulose and hemicellulose through hydrolysis of polysaccharides by bacteria and protozoa. This is then followed by microbial fermentation, generating hydrogen (H_2), CO_2 and, CH_4 as a byproduct (*10*). Production of CH_4 in ruminants is considered a loss of energy (*1*, *8*). Cattle typically lose 2-12% of their ingested energy as eructated CH_4 (*8*). Additionally, enteric CH_4 emissions from cattle show diurnal variation, maintaining higher concentrations during the day than at night, with the highest emissions occurring after feeding and during rumination events (*1*, *11*, *12*). Feed energy intake is the primary factor driving CH_4 emissions and is thought to be one of the best predictors of enteric gas production (*8*, *13*, *14*). Feed intake differs between dairy and beef cattle and contributes to observed differences in CH_4 emissions.

In addition to emissions from enteric fermentation, CH_4 is also produced during the decomposition of manure (*1*, *9*). Manure storage areas are the second largest contributors to CH_4 emissions on a commercial dairy (*15*). However, the relative contributions of stored manure to total CH_4 emitted from a dairy or feedlot is relatively (8-20%) small when compared to enteric fermentation values. Methane is emitted under anaerobic conditions during manure breakdown in systems such as: storage ponds, tanks, and pits where microorganisms are able to ferment organic materials (*10*, *15–17*). Methane emissions from manure storage areas are variable depending on management of the manure. Emissions can be affected by fecal matter excreted, physical form of the manure, excretal form of the waste, environmental conditions, and time elapsed before decomposition (*16*). There are also minor amounts emitted from barn floors or feedlots and following field application (*18*). Additionally, soil can actually absorb methane, but total amounts seems to be very small under typical conditions (*19*).

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

Nitrous Oxide

Nitrous oxide is a highly potent GHG; therefore, reducing N_2O emissions from U.S. beef and dairy production systems can have a significant impact on reducing overall GHG emissions from cattle production (*20*). Approximately 10% of the N_2O produced by agriculture originates from manure management on livestock facilities (*21*). The main sources of N_2O from cattle production systems are manure management (removal and storage of manure), chemical nitrogen (N) fertilizer, and animal manure applied to cropland and pasture

Nitrous oxide is a gaseous intermediate that is produced during the incomplete microbial processes of nitrification and denitrification. Nitrification is the aerobic microbial oxidation of ammonium (NH_4^+) to nitrate (NO_3^-), and denitrification is the anaerobic microbial reduction of NO_3^- to nitrogen gas (N_2) (*22*). Denitrification in manure storage areas and after incorporation of manure into the soil is considered the largest contributor of N_2O (*23*). Denitrification also occurs in slurry that contains NO_3^- from oxidizing NH_4^+ and in soils containing NO_3^- from chemical fertilizers or land application of manure (*10*). Ruminant animals are considered to contribute a small amount of N_2O emission from enteric fermentation (*9*, *10*, *12*). It is suspected that N_2O is also produced in the rumen as a byproduct of dissimilatory NO_3^- reduction to NH_4^+ (*9*). However, there is a scarcity of literature on enteric N_2O emissions from dairy cows (*1*). Animal treading and trampling on pastures could result in N_2O emissions, since animal treading reduces soil aeration, which leads to the anaerobic conditions conducive to denitrification (*16*, *24*).

Carbon Dioxide

In most GHG evaluations, CO_2 emitted from the respiration of cattle, microorganisms in manure, and human consumers is not considered a net contributor to climate change because the animals consume plants that fix CO_2 during photosynthesis (*25*). The CO_2 fixed during feed production is thus returned to the atmosphere by this respiration. Nevertheless, CO_2 emitted by modern cattle production systems from fossil fuel combustion for on-farm use, electricity generation, transportation, processing, and refrigeration has been considered a net source of GHGs in several LCAs (*7*, *26*, *27*) and whole-farm emissions models (*28*). However, the following discussion of direct sources of GHG from beef and dairy production will focus solely on the animal and its waste. Therefore, CO_2 mitigation from fossil fuel use will not be discussed.

Beef and Dairy Production Systems Effect on Greenhouse Gas Emissions

Greenhouse gas sources and their relative contributions from beef and dairy production systems are largely dependent on management. Variation in management techniques and producer objectives can result in different emission rates within cattle production systems. For example, a lactating beef cow is managed to produce adequate milk to wean a live calf; whereas, a lactating dairy cow is managed to maximize high quality milk production for human consumption. Although both cows are lactating, their metabolic rates and physiological needs differ, and thus, so do their emissions. The following sections will highlight these disparities in GHG emissions from beef and dairy production by focusing on extensive and intensive management systems.

Extensive Cattle Production

Extensive production refers to cattle that are raised on rangeland or pasture, and consume (through grazing) a high forage diet. Extensive cattle systems are unique because the animals graze non-arable land and convert this forage into a protein rich human food source. In the U.S. beef production system, this includes both the cow-calf and stocker operations. However, in some cases, steers are also finished on grass and those animals would also fall into this category.

Ruminants are known for their ability to digest fibrous plant material into usable energy. As mentioned previously, plant material is broken down through anaerobic fermentation by ruminant microbes to supply the animal with energy, microbial proteins, and the volatile fatty acids (VFA) acetate, proprionate, and butyrate (*29*, *30*). The primary substrates for methanogensis in the rumen are H_2 and CO_2. The H_2 is primarily produced through the formation of acetate and butyrate, which is favored by intake of roughage based diets (*31*). Therefore, cattle grazing on extensive rangelands produce more acetate and butyrate, and thus, have a larger H_2 pool. This results in the production of higher enteric CH_4 levels when compared to cattle on a high grain diet (*32–34*). Due to the nature of the high forage diets consumed through grazing on extensive operations, enteric derived CH_4 emissions from the cow-calf and stocker phases of beef cattle production contribute to a larger portion of total GHG emitted from the system, compared to enteric derived methane from a feedlot animal whom is managed intensively. Methane emissions from beef cattle in a pasture based system ranges from 85.92 to 259.9 g hd^{-1} d^{-1} depending on animal type, forage digestibility, and body weight (*35–39*) which is approximately double the amount of GHG emitted from cattle in feedlots. The large range in CH_4 emissions from pasture based beef production systems is indicative of the variation that is present in GHG emissions across different management schemes, forage quality, and cattle types.

In extensive systems, cattle waste is unmanaged as it is deposited directly on grazed land. The primary GHG emission source from manure deposited on grazed land is N_2O, which results from the N in animal waste (*40*). Often, the amount of N in the grazed legumes and grasses is higher than the animals' N (or protein) requirements. Thus, the unused N is primarily excreted as urea in the urine and a portion is emitted into the atmosphere through the denitrification process. Estimates suggest that cattle on pasture emit 0.1 to 0.7% of the N in feces and 0.1 to 3.8% of the N in urine into the atmosphere as N_2O (*41*). There is limited research on N_2O emissions from grazing cattle and more research needs to be conducted to improve our understanding of these GHG contributions. Nitrous oxide emissions vary greatly depending on the herbage N content, the soil type and condition, and animal compaction of the soil. Methane is also a source of GHG from unmanaged manure on grazed land; however, due to the aerobic conditions

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

that exist on pastures and ranges the overall contribution is less than 1-3 % of total grazed land GHG emissions (*34*, *40*).

Intensive Cattle Production

Intensive cattle production refers to animals that are raised in a more confined space, such as a feedlot or dairy, most often with feedstuff imports from outside the farm. Cattle raised intensively receive daily care. Typically, cattle in confined, intensive systems are fed formulated diets that meet their nutritional and physiological needs. In addition, the manure is managed from intense systems. These systems are managed to maximize milk and meat production and to maximize efficiencies. More specifically, feedlots are managed to maximize growth and carcass quality; while, dairies are managed to maximize milk production and milk quality.

Significantly more research has been conducted on GHG emission sources from intensive systems than that from extensive systems. The main GHG compounds from intensive systems are CH_4 from enteric fermentation and stored manure and N_2O from stored and land applied manure. Methane emissions from dairy animals is estimated to range from 3.1 to 8.3 % of gross energy intake (GEI) for dry cows and from 1.7 to 14.9 % of GEI for lactating cows (*42*). Lactating cows produce approximately 1.3 times more CH_4 than non-lactating (dry) cows (*12*). These emissions vary by stage of lactation and feeding level. Methane emissions from lactating cows range from 238 to 437 g cow^{-1} d^{-1} (*12*, *43*, *44*). Cattle on high grain diets (corn based), which are typically fed in commercial feedlots, are estimated to lose 3.5 % of GEI as CH_4 (*45*). Methane emissions from feedlot cattle fed high concentrate finishing diets range from 62 to 100 g hd^{-1} d^{-1} (*33*, *46*).

Manure management is critical for intensive cattle systems, because approximately 22-70 kg of feces and urine is produced daily by beef and dairy animals (*47*). Manure can either be stored in the dry (solid or semi-solid waste) or liquid form. Dairies typically utilize either solid or liquid management whereas feedlots manage their manure in solid form (*47*). Manure methane production is found to be highly variable across intensive operations, primarily because of the different diets fed (which affect the composition of manure, i.e. increased fermentable carbohydrates in feces from high-grain-fed animals), the varying environmental conditions (temperature and moisture), and the manure handling systems employed. Methane is the predominant GHG emitted from managed cattle waste, accounting for approximately 81% of the total emissions from manure (*40*). Nitrous oxide emissions from manure make up for the remaining 19% (*40*). Managed manure from dairy production systems produces more CH_4 emissions than managed manure stores from feedlots (*40*, *43*). While the literature is sparse, one estimate for dairy manure CH_4 is estimated at 140 g hd^{-1} d^{-1} with N_2O emissions at 16 g hd^{-1} d^{-1} (*43*).

Nitrous oxide emissions from stored manure depends on the manure storage condition (stacking density, water content, and temperature of the manure) (*11*, *48*, *49*). Waste management from feedlots differs slightly from dairies. In the feedlot, cattle are usually housed in drylots for 120-160 days depending on entry

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

weight, and manure is scraped from the drylot pens every 4-6 months or after every group rotation of animals. Therefore, a manure pack will develop. Research on manure pack emissions from feedlots show a strong positive correlation between CH_4 release and increasing nitrogen content of the manure (*50*). Additionally, CH_4 is released in greater quantities from the manure of housed (grain-fed) animals versus grazed animals (*50*). Methane and N_2O fluxes in feedlot manure packs range from 0.79-1.260 and 0.15-0.16 g hd^{-1} d^{-1}, respectively (*51*). Higher CH_4 emissions are associated with increased ambient temperatures (*52*, *53*) and manure temperatures (*54*).

Application of manure to soil as fertilizer can result in N_2O production. There are three main pathways that manure N will undergo after land application: 1) N is absorbed by the plants which is incorporated into plant protein, 2) N not absorbed by plants can be utilized by microbes to produce N_2O released into the atmosphere, and 3) NO_3^- leaching to the groundwater. In one study, N_2O emissions resulting from field application of manure were estimated to be 3.8 g m^{-3} manure slurry applied (*55*). It seems that N_2O emissions from field application are highest during the first 50 h after slurry application (*56*). The N_2O emissions from land application are driven by carbon and nitrogen substrate availability, temperature, pH, aeration, and moisture. Targeting these environmental drivers are possible avenues for mitigation of N_2O from dairies and feedlots. Additionally, manure application methods and soil condition have significant impacts on N_2O emissions from manure applied soil.

Life Cycle Assessment

Quantifying GHG emission sources from U.S. beef and dairy cattle production systems is complex and challenging due to the variation across farms, ranches, and feedlots. To accurately evaluate the true GHG contribution of these independent cattle systems, an LCA must be used. The LCA tool should be supported with extensive field work to achieve accurate results. Assumptions in the LCA should be specific to cattle type, management strategy, and region. For example, cattle raised in the U.S. should not be compared to cattle raised in a third world country using the same assumptions. Life cycle assessments are most accurate when assumptions are created for systems in specific regions and adjusted to meet those management techniques.

Estimation of total global GHG contributions from beef and dairy cattle was attempted by the United Nations, Food and Agriculture Organization in the report, Livestock's Long Shadow. This report suggested that 18% of total anthropogenic GHGs were caused by livestock, more than global transportation contribution to anthropogenic GHGs (*7*). This estimated contribution is in stark contrast to the U.S. specific LCA performed by the Environmental Protection Agency (EPA) that suggests livestock contributes less than 3% of total anthropogenic GHGs (*57*). This demonstrates the need for LCAs that are specific to animal type and climate to fully understand the true sources and contributions of livestock to climate change.

Ultimately, every GHG source and mitigation strategy should be evaluated and implemented in conjunction with other environmental (water and soil), animal welfare, and economic strategies. Additionally, development of GHG reducing technologies should consider consumer acceptance and product marketability. Taking a holistic approach to GHG emission sources and mitigation techniques is necessary to ensure the continuation of sustainable food production.

References

1. Jungbluth, T.; Hartung, E.; Brose, G. *Nutr. Cycl. Agroecosys.* **2001**, *60* (1), 133–145.
2. USDA National Agriculture Statistics http://www.nass.usda.gov/ (accessed November 20, 2010).
3. Lowe, M.; Gereffi, G. A Value Chain analysis of the U.S. Beef and Dairy Industries; Center on Globalization, Governance, & Competitiveness; Duke University. Report prepared for the Environmental Defense, 2009.
4. New Jersey Agricultural Experiment Station, Rutgers. Animal Waste Management. http://njaes.rutgers.edu/animal-waste-management/ (accessed December 6, 2010).
5. Jones, D.; Sutton, A. CAFOs: Concentrated Animal Feeding Operations. Manure Storage Systems, ID-352; Purdue Extension, Purdue University: 2007.
6. Natural Resources Conservation Service. Fact sheet: Anaerobic Digester-Controlled Temperature. 2006. http://www.mi.nrcs.usda.gov/technical/engineering/animal_waste.html (accessed December 3, 2010).
7. Steinfeld, H.; Gerber, P.; Wassenaar, T.; Castel, V.; Rosales, M.; Haan, C. D. Livestock's long shadow: environmental issues and options Food and agriculture Organization of the United Nations: Rome, 2006.
8. Johnson, K. A.; Johnson, D. E. *J. Anim. Sci.* **1995**, *73* (8), 2483–2492.
9. Kaspar, H. F.; Tiedje, J. M. *Appl. Environ. Microbiol.* **1981**, *41* (3), 705–709.
10. Monteny, G. J.; Groenestein, C. M.; Hilhorst, M. A. *Nutr. Cycl. Agroecosys.* **2001**, *60* (1), 123–132.
11. Amon, B.; Amon, T.; Boxberger, J.; Alt, C. *Nutr. Cycl. Agroecosys.* **2001**, *60*, 103–113.
12. Sun, H.; Trabue, S. L.; Scoggin, K.; Jackson, W. A.; Pan, Y.; Zhao, Y.; Malkina, I. L.; Koziel, J. A.; Mitloehner, F. M. *J. Environ. Qual.* **2008**, *37* (2), 615–22.
13. Mills, J. A. N.; Kebreab, E.; Yates, C. M.; Crompton, A.; Cammell, S. B.; Dhanoa, M. S.; Agnew, R. E.; France, J. *J. Anim. Sci.* **2003**, *81*, 3141–3150.
14. Ellis, J. L.; Kebreab, E.; Odongo, N. E.; McBride, B. W.; Okine, E. K.; France, J. *J. Dairy Sci.* **2007**, *90* (7), 3456.
15. Sneath, R. W.; Beline, F.; Hilhorst, M. A.; Peu, P. *Agric. Ecosys. Environ.* **2006**, *112*, 122–128.
16. Saggar, S.; Bolan, N. S.; Bhandral, R.; Hedley, C. B.; Luo, J. *N. Z. J. Agric. Res.* **2004**, *47*, 513–544.
17. Olesen, J. E.; Schelde, K.; Weiske, A.; Weisbjerg, M. R.; Asman, W. A. H.; Djurhuus, J. *Agric. Ecosys. Environ.* **2006**, *112* (2-3), 207–220.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

18. Chianese, D. S.; Rotz, C. A.; Richard, T. L. *Appl. Eng. Agric.* **2009**, *25*, 431–442.
19. Rotz, C. A.; Montes, F.; Chianese, D. S. *J. Dairy Sci.* **2010**, *93*, 1266–1282.
20. Intergovernmental Panel on Climate Change (IPCC). Fourth Assessment Report AR4, 2007. http://ipcc-wg1.ucar.edu/index.html.
21. United States Environmental Protecton Agency (USEPA); Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2008; U.S. EPA # 430-R-10-006; Washington DC., 2010, URL http://www.epa.gov/climatechange/emissions/usinventoryreport.html.
22. Moiser, A. R.; Kroeze, C.; Nevison, C.; Oenema, O.; Seitzinger, S.; Cleemput, O. V. *Nutr. Cycl. Agroecosys.* **1998**, *52*, 225–248.
23. Wagner-Riddle, C.; Kebreab, E.; France, J.; Clark, H.; Rapai, J. In Supporting measurements required for evaluation of greenhouse gas emission models for enteric fermentation and stored animal manure, 2nd Meeting of the Animal Production and Manure Management Network, Canada, 2006.
24. Meneer, J. C.; Ledgard, S.; McLay, C.; Silvester, W. *Soil Biol. Biochem.* **2005**, *37*, 1625–1629.
25. Pitesky, M. E.; Stackhouse, K. R.; Mitloehner, F. M. *Adv. Agron.* **2009**, *103*, 1–40.
26. Casey, J. W.; Holden, N. M. *J Environ. Qual.* **2005**, *34* (2), 429–36.
27. Capper, J. L.; Cady, R. A.; Bauman, D. E. *J. Anim. Sci.* **2009**, *87* (6), 2160–2167.
28. Schils, R. L. M.; Olesen, J. E.; del Prado, A.; Soussana, J. F. *Livest. Sci.* **2007**, *112* (3), 240–251.
29. Hungate, R. E. In *The rumen bacteria. The rumen and its microbes*; Academic Press: New York, 1996.
30. Russell, J. B.; Rychilk, J. L. *Science* **2001**, *292*, 1119–1122.
31. Moe, P. W.; Tyrell, H. F. *J. Dairy Sci.* **1979**, *62*, 1583–1586.
32. Lovett, D.; Lovell, S.; Stack, L.; Callan, J.; Finlay, M.; Conolly, J.; O'Mara, F. P. *Livest. Prod. Sci.* **2003**, *84* (2), 135–146.
33. Beauchemin, K. A.; McGinn, S. M. *J. Anim. Sci.* **2005**, *83* (3), 653–661.
34. Kebreab, E.; Clark, K.; Wagner-Riddle, C.; France, J. *Can. J. Anim. Sci.* **2006**, *86* (2), 135–158.
35. Pavao-Zuckerman, M. A.; Waller, J. C.; Ingle, T.; Fribourg, H. A. *J. Environ. Qual.*, *28* (6), 1963–1969.
36. Laubach, J.; Kelliher, F. M.; Knight, T. W.; Clark, H.; Molano, G.; Cavanagh, A. *Aust. J. Exp. Agric.* **2008**, *48*, 132–137.
37. DeRamus, H. A.; Clement, T. C.; Giampola, D. D.; Dickison, P. C. *J. Environ. Qual.* **2003**, *32*, 269–277.
38. Hart, K. J.; Martin, P. G.; Foley, P. A.; Kenny, D. A.; Boland, T. M. *J. Anim. Sci.* **2009**, *87*, 3342–3350.
39. Harper, L. A.; Denmead, O. T.; Freney, J. R.; Byers, F. M. *J. Anim. Sci.* **1999**, *77*, 1392–1401.
40. United States Department of Agriculture, U.S. Agriculture and Forestry Greenhouse Gas Inventory. Chapter 2: Livestock and Grazed Land Emissions. 1990-2005; pp 11−32.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

41. Oenema, O.; Velthof, G. L.; Yamulki, S.; Jarvis, S. C. *Soil Use Manage.* **1997**, *13*, 288–295.
42. Holter, J. B.; Young, A. J. *J. Dairy Sci.* **1992**, *75*, 2165–2175.
43. Phetteplace, H. W.; Johnson, D. E.; Seidl, A. F. *Nutr. Cycl. Agroecosys.* **2001**, *60* (1-3), 99–102.
44. Grainger, C.; Clarke, T.; McGinn, S. M.; Auldist, M. J.; Beauchemin, K. A.; Hannah, M. C.; Waghorn, G. C.; Clark, H.; Eckard, R. J. *J. Dairy Sci.* **2007**, *90* (6), 2755–66.
45. Intergovernmental Panel on Climate Change (IPCC) Greenhouse gas inventory reference manual. IPCC guidelines for national greenhouse gas inventories. Geneva, 1996.
46. Stackhouse, K. S.; Zhao, Y.; Pan, Y.; Mitloehner, F. M. *J. Environ. Qual.* In press.
47. Davis, J. G.; Stanton, T. L.; Haren, T. *Management. Feedlot manure management*; Colorado State Univeristy Cooperative Extension: Fort Collins, 2002.
48. Dewes, T. *J. Agric. Sci.* **1996**, *127* (4), 501–509.
49. Webb, J.; Chadwick, D.; Ellis, S. *Nutr. Cycl. Agroecosys.* **2004**, *70* (1), 67–76.
50. Jarvis, S. C.; Lovell, R. D.; Panayides, R. *Soil Biol. Biochem.* **1995**, *27* (12), 1581–1588.
51. Boadi, D. A.; Wittenberg, K. M.; Scott, S. L.; Burton, D.; Buckley, K.; Small, J. A.; Ominski, K. H. *Can. J. Anim. Sci.* **2004**, *84* (3), 445–454.
52. Kaharabata, S. K.; Schuepp, P. H.; Desjardins, R. L. *Environ. Sci. Technol.* **2000**, *34* (15), 3296–3302.
53. Massé, D. I.; Croteau, F.; Patni, N. K.; Masse, L. *Can. Biosyst. Eng.* **2003**, *45*, 3.1–6.6.
54. Husted, S. *J. Environ. Qual.* **1994**, *23*, 585–592.
55. Amon, B.; Kryvoruchko, V.; Amon, T.; Zechmeister-Boltenstern, S. *Agric. Ecosys. Environ.* **2006**, *112*, 153–162.
56. Clemens, J.; Huschka, A. *Nutr. Cycl. Agroecosys.* **2001**, *59*, 193–194.
57. Hockstad, L.; Weitz, M. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2007. Environmental protection Agency, Washington DC; 2009; 430-R-09-004.

Downloaded by PENNSYLVANIA STATE UNIV on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch021

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Chapter 22

Greenhouse Gas Emissions from Cattle Feedlot Manure Composting and Anaerobic Digestion as a Potential Mitigation Strategy

Brandon Gilroyed, Xiying Hao,[*] Francis J. Larney, and Tim A. McAllister

**Agriculture and Agri-Food Canada, Lethbridge Research Centre,
5403-1st Avenue South, Lethbridge, Alberta, Canada T1J 4B1
[*]E-mail: xiying.hao@agr.gc.ca. Phone: 403-317-2279. Fax: 403-317-2187.**

Livestock production is a significant source of greenhouse gas (GHG) emissions, and the management of livestock manure is responsible for approximately 3% of CH_4 and 12% of total N_2O emissions in Canada. Composting is a manure management strategy that reduces the impact of land applied manure to the environment. However, nitrogen loss and GHG emissions are known to occur during the composting process. Anaerobic digestion is an alternative manure management strategy that can be utilized in conjunction with composting to limit nitrogen loss and reduce GHG emissions. A discussion focused on comparing different manure management strategies, the biological mechanisms at work in each, and their impact on GHG emissions will be undertaken in this chapter.

Introduction

Emission of greenhouse gases (GHG), such as CH_4 and N_2O, is a major contributing factor to global warming (*1*). Worldwide livestock numbers are growing as per capita meat consumption is projected to double from 1964-1966 levels by 2030 (*2*), increasing the significance of animal production systems on GHG emissions (*3*, *4*). Currently, animal production systems are responsible for contributing up to 18% of total global GHG emissions (*5*), including approximately 5-30% of total CH_4 and 7-18% of total N_2O (*6–10*). Livestock manure management specifically contributes 30-50% of total agricultural N_2O

Published 2011 by the American Chemical Society
In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

emissions (*11*), and 12-41% of total agricultural CH_4 emissions depending on the country considered (*12*).

The main greenhouse gases associated with livestock manure management are CH_4 and N_2O, which exhibit global warming potentials of 25 and 298 times that of CO_2 over a 100 year time horizon (or 72 and 289 times that of CO_2 over a 20 year time horizon) (*13*). In addition to its global warming potential, N_2O can also adversely affect the ozone layer. The photochemical decomposition of N_2O into NO results in depletion of stratospheric ozone (*14*), causing increased levels of ultraviolet (UV) radiation to reach the earth's surface (*15*). Methane oxidized by hydroxyl radicals in the troposphere increases tropospheric ozone levels, which enhances the greenhouse effect (*15*). Although significant amounts of CO_2 are produced during livestock manure management, this is considered GHG neutral because mineralization to CO_2 and H_2O is the optimal fate of all organic matter (*16*). As such, efforts to reduce GHG emissions from livestock manure are focused on CH_4 and N_2O.

Livestock manure management can be considered as a continuum, beginning with manure production from animals, proceeding to storage and treatment, and culminating in land application (*12*). Within this continuum, manure management can be approached in two ways: either the manure is immediately applied directly to a field, or more typically, it is stored in some way prior to land application. If fresh manure is applied directly to land, CH_4 production is negligible, particularly in comparison to manure storage, but emission of N_2O is prevalent (*17*). Fresh manure has a high moisture content, making transport away from intensive production areas costly. This in turn leads to over-application of raw manure to land immediately adjacent to production areas, which introduces problems with nutrient leaching and runoff into water resources (*18*). If manure is stored prior to land application, there are generally four different options available, each with its own advantages and disadvantages (Table I). The manure can be stockpiled, stored as slurry, composted, or anaerobically digested. For a review on the implications of different manure management strategies on GHG emissions, see Chadwick et al. (*12*). In the future, on farm disposal options for other types of agricultural wastes could also affect manure management practices. For example, disposal of animal mortalities (*19–21*), specified risk materials (*22*), or other agricultural wastes by co-composting with livestock manure or by anaerobic digestion (*23*, *24*) would affect the GHG emission potential due to greater availability of readily degradable organic matter. In the last decade, composting has gained a foothold in the cattle feedlot industry in southern Alberta as an alternative to land spreading of fresh manure (*25*, *26*). Composting decreases manure volume (*27*), and reduces or eliminates coliform bacteria (*28*), human parasites (*29*), plant pathogens (*30*), and weed seed viability (*31*). Despite its benefits, like most manure-handling or storage practices, composting is associated with N and C losses, some of which are in the form of GHG (*32*, *33*).The focus of this discussion will be on GHG emission from composting livestock manure. Other manure management options such as anaerobic digestion and land application will also be briefly discussed.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Table I. Advantages and disadvantages of different manure management strategies with a focus on greenhouse gas emission potential

Manure Management Strategy	Advantages	Disadvantages
Direct Land Application	No CH_4 emission Inexpensive Non-technical Enhanced sequestration of soil C Improve soil fertility	Time- manure storage is often necessary Nitrate leaching into groundwater N_2O emission Phosphate runoff into surface water Malodour No pathogen reduction Transportation costs
Manure Stockpiling	Inexpensive Non-technical	Highest GHG emissions Minimal pathogen reduction
Slurry	Automated Moderately expensive	Second highest GHG emissions Malodour High water content/low dry matter content Minimal pathogen reduction Semi-technical Water pollution
Compost	Inexpensive Organic fertilizer production Enhanced sequestration of soil C Improve soil fertility Malodour reduction Pathogen reduction Pest/weed reduction	Moderate CH_4 and N_2O emission Semi-technical N loss due to NH_3 emission Land requirement (compact earthen pad/catch basin) for compost site
Anaerobic Digestion	No GHG emission Renewable energy production Organic fertilizer production Malodour reduction Pathogen reduction	Expensive infrastructure Technical Economies of scale

Biological Mechanisms of GHG Production During Composting

Greenhouse gas production during composting is primarily the result of the microbiological breakdown of organic matter. Under aerobic conditions, organic matter is broken down into CO_2 and H_2O by the activities of a variable

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

microbial consortium (including bacteria, archaea, and fungi) in a series of complex biological reactions. Part of the energy produced during these reactions is lost as heat and the remainder is used for cellular growth. Depending on the chemical composition of the substrate, complete mineralization to CO_2 and H_2O may not be possible, at least during a short enough time frame to be of practical use. For example, total degradation of complex polymers such as lignin, cellulose, or hemicellulose is unlikely to be complete even after several years, which contributes to carbon sequestration in soils over time (*34*).

Under anaerobic conditions, the degradation of organic matter results in methanogenesis via the combined activity of three distinct groups of microbes (Figure 1) (*35*). Complex polymers are reduced to monomers via extracellular enzymes produced, and subsequently those monomers are fermented into organic acids, alcohols, H_2, and CO_2 by the activity of fermentative bacteria. Acetogenic bacteria convert larger organic acids to acetic acid and H_2, which in turn are converted to CH_4 by the action of either acetoclastic (eqn. 1) or hydrogenotrophic methanogenic archaea (eqn. 2) (*36*). Methylotrophic production of CH_4 from C1 compounds is also possible, but will not be discussed here (*35*). Methanogenesis does not occur, or at least is reduced, if alternate electron acceptors, such as sulphate, nitrate, Mn(IV), or Fe(III) are available (*37*).

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 \qquad \Delta G_O = -76\ kJ\ mol^{-1} \qquad \text{eqn. 1}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta G_O = -131\ kJ\ mol^{-1} \qquad \text{eqn. 2}$$

Methanogens are slow growing, obligately anaerobic organisms with optimal growth at or near neutral pH. In compost, methanogenic activity is optimal within a pH range of 6.8-7.4 (*38*). The presence of oxygen or a $pH < 6$ is lethal to methanogens (*39*, *40*). However, they are able to survive and remain active over a wide temperature range, from psychrophilic conditions (<20°C) to thermophilic (<70°C) (*41*, *42*).

A group of obligately aerobic bacteria, comprised of 13 genera among the γ (Type I) and α (Type II) Proteobacteria and known collectively as methanotrophs (*43*), are able to utilize CH_4 as an energy source (*44*). Beginning with the activity of the methane monooxygenase enzyme, CH_4 is converted to methanol (eqn. 3). Formaldehyde produced from the oxidation of methanol (eqn. 4) can be fed into the ribulose monophosphate pathway (Type I) or the serine isocitrate lyase (Type II) pathway (Type II) (*45*). Otherwise, formaldehyde is converted to formic acid (eqn. 5), which is subsequently converted to CO_2 (eqn. 6).

$$CH_4 + NADH + H^+ + O_2 \rightarrow CH_3OH + NAD^+ + H_2O \qquad \text{eqn. 3}$$

$$CH_3OH + \text{methoxatin} \rightarrow CH_2O + \text{methoxatin (reduced)} \qquad \text{eqn. 4}$$

$$CH_2O + NAD^+ + H_2O \rightarrow HCOOH + NADH + H^+ \qquad \text{eqn. 5}$$

$$HCOOH + NAD^+ \rightarrow CO_2 + NADH + H^+ \qquad \text{eqn. 6}$$

Methanotrophic bacteria also exist in soil and they are sensitive to the presence of a variety of chemicals, including herbicides and fertilizers (*46*, *47*). In a study examining methanotrophic community dynamics in compost, Type I methanotrophs were predominant and species diversity was inversely correlated to compost temperature (*45*). It should be noted that low levels of CH_4 were produced in the Halet et al. (*45*) study, which favours Type I methanotrophs over Type II (*48*)(*49*), but that this may not be the situation in all compost piles. Methane oxidation can also be performed under anaerobic conditions by the actions of sulphate reducing bacteria and some archaea, although the importance of these processes is not yet well understood (*50*). Methane emission during composting is therefore not only a function of the rate of CH_4 production by methanogens but also the rate of CH_4 consumption by methanotrophs (*51*).

Nitrous oxide is a byproduct of nitrification (autotrophic or heterotrophic), denitrification, and nitrifier denitrification (*52*). In the case of autotrophic nitrification, NH_4^+ is converted to NO_2^- in a two-step process by the joint activity of ammonia oxidizing bacteria (AOB) (e.g., *Nitrosomonas*) and nitrite oxidizing bacteria (NOB) (e.g., *Nitrobacter*) under aerobic conditions (Figure 2A). Ammonia oxidation by certain archaea (AOA) has also been reported, and their contribution may be greater than bacterial ammonia oxidizers within certain ecological niches (*53*, *54*). In one study, the estimated population of AOA was greater than that of AOB, suggesting a strong role for AOA, particularly later in the composting process when temperatures and NH_4^+ concentrations are reduced (*55*). Ammonia monooxygenase, which catalyzes the oxidation of NH_3 to NH_2OH, has a wide substrate specificity and can be inhibited by non-target substrates (e.g., acetylene) through competition or covalent binding to the active site of the enzyme. Hydroxylamine oxidoreductase catalyzes the oxidation of NH_2OH to NO_2^-, and during this reaction N_2O can be produced as a byproduct by chemical decomposition (caused by organic or inorganic compounds, particularly at low pH) of NH_2OH or NO_2^- (*56*) or due to incomplete oxidation of NH_2OH (*52*, *57*, *58*). The oxidation of NO_2^- to NO_3^- is performed by NOB through the enzymatic activity of nitrite oxidoreductase. High concentrations of NH_3 are toxic to NOB such as *Nitrobacter* (*52*). In general, AOB and NOB are slow growing because of the poor energy return realized from using NH_3 and NO_2^-, respectively, as substrates. To produce 1 g of dry microbial biomass, 30 g of NH_3 must be consumed (*59*), which indicates even a small nitrifier population can have significant impact on NH_3 conversion to NO_3^- and byproducts such as N_2O.

Heterotrophic nitrification is more prevalent in fungi than bacteria, but some heterotrophic bacteria have the ability to nitrify, and some can even denitrify under aerobic conditions (*60*). Although heterotrophic nitrifiers produce more N_2O per cell than autotrophic nitrifiers (*61*, *62*), they are typically not considered a major source of N_2O. Under certain conditions (e.g., low pH, high O_2 concentration, plentiful organic C), the importance of heterotrophic nitrification could be increased (*52*).

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

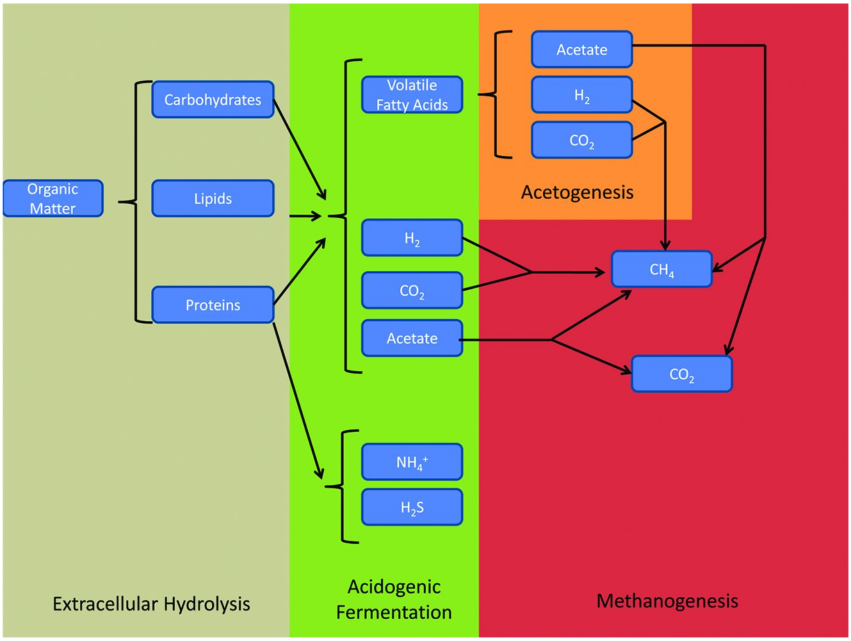


Figure 1. The anaerobic degradation of organic matter can be divided into four stages which are undertaken by three different groups of bacteria. Initial hydrolysis of complex organic matter (i.e., proteins degraded to amino acids, carbohydrates to sugars, lipids to fatty acids) and fermentation of monomeric components to produce volatile fatty acids (VFA), CO_2, H_2, acetate, NH_4^+ and H_2S is performed by the first bacterial group. Acetogenesis is the conversion of VFA to acetate, H_2, and CO_2, and is performed by the second group. The final group of methanogens produces CH_4 either by splitting acetate or combining CO_2 with H_2.

Denitrification is the anaerobic reduction of NO_3^- to N_2, and the process is performed by a diverse group of bacteria (*63*). Dissimilatory denitrification resulting in N_2O formation can also be performed by certain fungi under anoxic conditions (*64*), but will not be discussed in detail here. Denitrifying bacteria are typically heterotrophic, facultative anaerobes. Nitrous oxide is a direct intermediate in the reduction pathway of NO_3^- (Figure 2B). Any disruption in the denitrification pathway can therefore lead to the emission of N_2O. For example, nitric oxide reductase is inhibited at low pH, which would allow accumulation and emission of N_2O (*65*). If the concentration of NO_3^- is high, reduction of N_2O is decreased as NO_3^- is the preferred electron acceptor (*59*). If oxygen is present in sufficient concentration, denitrification will stop. But under limited O_2 conditions, N_2O emission can be enhanced because nitrous oxide reductase is more easily inhibited by O_2 than the other enzymes in the pathway (*52*). This effectively makes N_2O the end product of denitrification. Although nitrification is an aerobic process and denitrification is an anaerobic process, the two processes can be coupled in environments where an aerobic/anaerobic interface exists (*66*). In this situation, NO_3^- produced during nitrification is utilized by denitrifiers to produce N_2.

In coupled nitrification/denitrification, three distinct bacterial groups are involved in the conversion of NH_3 to N_2. However, in nitrifier denitrification, the entire process occurs in a single organism, which is an autotrophic NH_3 oxidizer (Figure 2C) (*67*). In contrast to coupled nitrification/denitrification, this process does not ever produce NO_3^-. The ecological niche for nitrifying denitrifiers likely requires low O_2 concentration, abundance of N, limited C, and possibly lower pH (*52*). The importance of nitrifier denitrification in emission of N_2O from soil environments varies widely in the literature, from insignificant (*68*) to 30% of total N_2O emission (*69*). Determining the ratio of N_2O emission caused by nitrification vs. denitrification vs. nitrifier denitrification is difficult due to the interdependence of the groups (*70*).

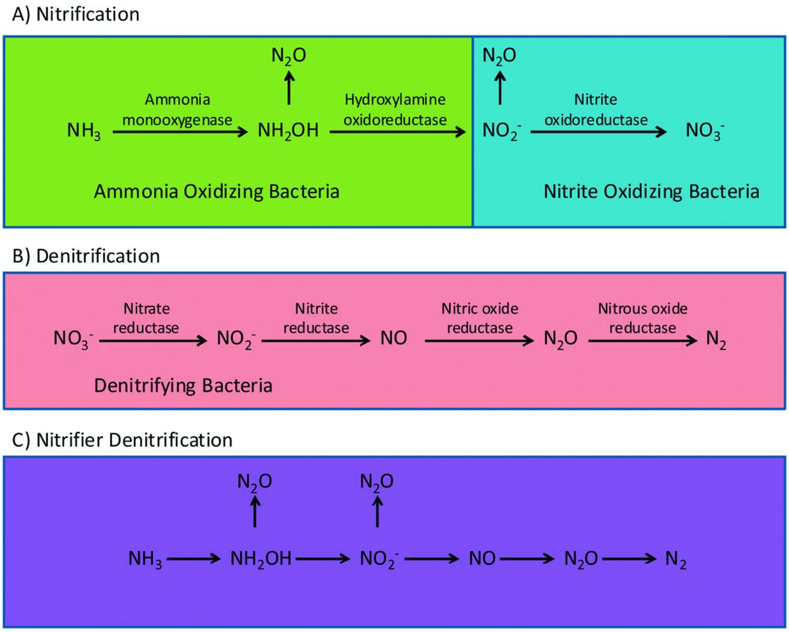

A) Nitrification
N2O
NH3
Ammonia monooxygenase
NH2OH
Hydroxylamine oxidoreductase
N2O
NO2-
Nitrite oxidoreductase
NO3-
Ammonia Oxidizing Bacteria
Nitrite Oxidizing Bacteria
B) Denitrification
NO3-
Nitrate reductase
NO2-
Nitrite reductase
NO
Nitric oxide reductase
N2O
Nitrous oxide reductase
N2
Denitrifying Bacteria
C) Nitrifier Denitrification
N2O
N2O
NH3
NH2OH
NO2-
NO
N2O
N2

Figure 2. The processes of nitrification (A), denitrification (B), and nitrifier denitrification (C). Nitrification requires the activity of two different bacterial groups, represented by the separated boxes. At anoxic interfaces where the processes of nitrification and denitrification can both proceed, NO_3^- produced by nitrifiers can be consumed by denitrifiers. In nitrifier denitrification, both processes take place in a single organism.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Typical GHG Emission Patterns from Compost

The composting process has multiple phases which succeed each other over time (Figure 3). Substrate availability is highest at the start of composting, which leads to a rapid increase in microbial activity. Substrate degradation, CO_2 emission, and compost pile temperature are directly correlated (*16*, *71*). Because heat is a byproduct of microbial metabolism, the compost pile temperature increases to thermophilic levels quickly (e.g., 70°C within 24 h of compost windrow establishment). Over time the amount of substrate available for metabolism decreases, causing a reduction in microbial activity and heat production. This gradual reduction in temperature shifts the compost pile from thermophilic to mesophilic. If the compost pile is turned to increase aeration, a temporary increase in temperature can be expected. The temporal changes in compost pile temperature and organic matter composition leads to microbial community succession (*72*, *73*). Bacteria dominate the thermophilic phase while the prevalence of fungi increases as temperatures are reduced to mesophilic or ambient levels. The heating pattern of compost piles produces a "chimney effect" in which an efflux of heated air exits at the top of the pile, while fresh air is brought into the pile from the bottom and sides (*16*, *74*). As such, most GHG emissions occur from the top of the pile and not the sides (*75*).

Another result of the high initial microbial activity is that O_2 is rapidly consumed, leading to the formation of anaerobic zones within the compost pile (Figure 4). Because O_2 is consumed during aerobic degradation of organic matter, O_2 concentration within the compost pile will decrease during the thermophilic phase of composting. In areas where little or no O_2 is present, anaerobic degradation of organic material occurs. Unlike aerobic degradation, which primarily yields CO_2 and H_2O, anaerobic degradation primarily results in CH_4 production by the activity of methanogens (Figure 1). As mentioned previously, methanogens are sensitive to O_2 and are only active under strictly anaerobic conditions. Such conditions occur temporally early in the composting process when microbial activity and O_2 consumption are at their peak, and spatially deep within the compost pile (*32*). Emission of CH_4 from compost piles is therefore found predominantly at the beginning of the composting process and is negligible as microbial activity decreases later on (Figure3) (*32*, *76*).

Methanotrophic activity reduces the amount of CH_4 emitted from compost, oxidizing CH_4 as it moves upward from anaerobic zones within the pile due to the "chimney effect" (*74*). Methanotrophic microbes have been detected in compost piles both near the surface and near the middle, suggesting their activity could have a broad spatial range within the pile (*77*). However, CH_4 emission can still occur for two main reasons. The first is that as the peak of CH_4 production occurs shortly after the initial start of the composting process, the methanotrophic community does not have adequate time to become established, allowing some CH_4 to escape out of the pile. The second reason is that methanotrophic oxidation of CH_4 is not completely efficient, so at peak CH_4 production some will be emitted.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

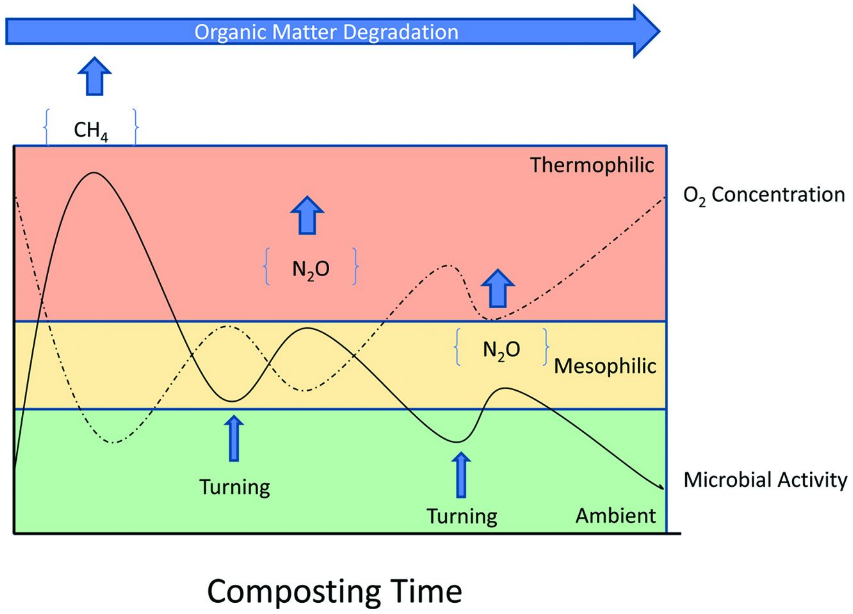
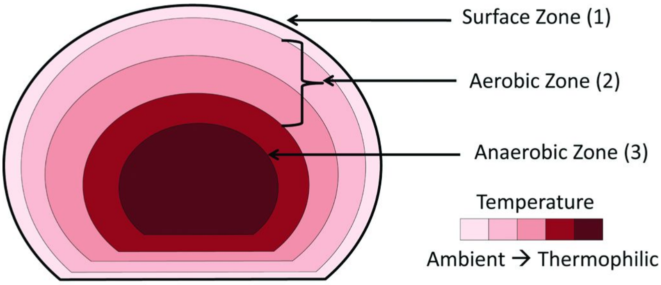


Figure 3. Typical pattern of microbial activity, temperature profile, oxygen concentration, and greenhouse gas emissions over time during composting. Thermophilic temperatures are rapidly achieved due to microbial degradation of organic matter which consumes oxygen and results in anaerobic zones where CH_4 production can occur via methanogenesis. Over time the temperature declines to mesophilic levels, enabling the growth of nitrifying bacteria which may cause N_2O emission. After turning events, NO_2^- accumulated in the surface layer of compost can be mixed down into anaerobic zones of the pile, causing N_2O emission due to denitrification.

Emission of N_2O from compost piles varies according to manure source and management strategies. When composting animal manures, N_2O emissions typically represent approximately 5% of total N loss (*78*, *79*). Depending on compost management, N-loss due to N_2O can range from <1% to >6% (*80*). Emission of N_2O from compost is primarily due to two different processes. The first is nitrification, which occurs near the aerobic outer surface of the compost pile (Figure 2). Nitrification occurs near the compost surface, where O_2 concentrations are highest (*79*). The activity of autotrophic nitrifying bacteria is typically considered to be inhibited at temperatures above 40°C (*81*), so N_2O emissions due to their activity typically occur either immediately after the compost process starts, but before thermophilic phase, or after the temperature has receded to mesophilic levels (*16*, *79*). The existence of thermophilic ammonia oxidizing bacteria has been reported in compost, though their importance in the nitrogen cycle within compost piles is not well studied (*82*). Ammonia oxidation increases rapidly during the first days of composting, reducing NH_3 emissions (*83*). The second primary source of N_2O emission occurs immediately after pile construction (if NO_2^- had accumulated in the manure to be composted during

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

storage) or after compost turning has occurred (*84*, *85*). In this scenario, NO_3^- produced through nitrification near the compost surface is mixed down into the middle of the compost pile, which may be anaerobic. Anaerobic conditions foster denitrification, which can produce N_2O if not completed (see discussion above). Additionally, leaching of highly mobile NO_3^- from the top layer down into anaerobic zones can result in N_2O emissions from incomplete denitrification (*22*, *78*). Of the two processes, nitrification near the surface of the compost pile is responsible for the majority of N_2O emissions from compost piles according to some studies, and this emission is tightly correlated to accumulation of NO_2^- (*76*, *86*). However, other studies suggest that the majority of N_2O emission occurs as a result of denitrification immediately after turning events (*70*). Reduction of N_2O to N_2 is reported to occur sparsely throughout the composting process (*70*).



Process	Primary Products	Zone	Conditions
Aerobic Organic Matter Degradation	CO_2, H_2O, NH_4^+	1,2	Requires O_2
Anaerobic Organic Matter Degradation	CH_4, CO_2	2,3	Absence of O_2
Nitrification	NO_3^-, N_2O	1	Requires O_2, NH_3
Denitrification	N_2, N_2O	3	Requires NO_2^-
Nitrifier Denitrification	N_2, N_2O	1	Low O_2, high N, low C
Methanotrophy	CO_2	1,2	Requires O_2

Figure 4. Spatial profile of the oxygen gradient found in compost. At the center of the pile, oxygen concentration would be lowest, leading to the formation of anaerobic zones. Near the compost pile surface, aerobic conditions would exist. The area between the aerobic surface and the anaerobic center is a heterogeneous gradient. At anoxic interfaces, the activities of aerobic and anaerobic microbes may be in contact with one another. Although certain processes are typically associated with particular locations in the pile, the heterogeneity of compost makes exact spatial allocation of these activities imprecise.

Emission of GHGs from compost is highly variable, even when considering similar substrate types (e.g., cattle manure) (*87*). Given heterogeneity in the substrate itself as well as the impact of environmental factors, GHG emission patterns and total emissions can vary widely (Table II). The diet of animals affects the composition of their manure, which in turn can alter GHG emissions during composting. For example, beef cattle fed dried distillers' grains and solubles (DDGS) have higher concentrations of NH_4^+-N in their manure, which subsequently leads to increased N_2O emissions during composting (*88*). The presence of trace chemicals, such as antibiotics, can alter the microbial community composition and potentially affect the compost process (*87*).

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Managing Compost Conditions for Minimizing GHG Production

As discussed previously, the most important factor for limiting GHG emissions from compost is to limit the formation of anaerobic zones which are responsible for CH_4 production and denitrification-based N_2O production. Many factors can contribute to the formation of anaerobic areas, including moisture content, bulk density, manure composition, pH, compost pile size and dimensions, and turning frequency (*71*, *89*). Over time organic matter degradation leads to compaction of the pile, reducing pore space and making aeration more difficult until the pile is turned (*90*). A variety of strategies can be employed to manage the conditions responsible for GHG emissions during composting. In general, compost can either greatly reduce (-900 kg CO_2 equivalent (eq.) tonne^{-1} waste) or be a source (+300 kg CO_2 eq. tonne^{-1} waste) of GHG depending on the efficacy of the strategies employed and the costs of various inputs (*91*).

The overall size and dimensions of the compost pile can be manipulated to maximize O_2 concentration within the pile. In general a larger compost pile will emit more CH_4 than a smaller compost pile, as increasing pile size also increases the likelihood of anaerobic zones developing, spurring CH_4 formation (*79*, *92*, *93*). As the compost pile matures, anaerobic zones will decrease in size and eventually disappear, but in larger piles this zone will persist for a longer period of time (*94*). It should also be noted that increasing piles increases the heterogeneity of GHG emissions, making accurate measurements more difficult (*93*). Bench scale composters may not emit any CH_4 at all (*95*), but such small piles are not possible at industrial scale. Large piles emit more total N_2O, and do so over a longer period of time, than a smaller pile (*79*). Increasing the compost pile's ratio of surface area to volume will also reduce the formation of anaerobic zones. For conically shaped compost piles, the volume of anaerobic zones increases logarithmically against the volume of aerobic zones as pile size increases (*79*). Utilizing smaller compost piles in conjunction with more frequent turning can reduce GHG emissions by maintaining aerobic conditions (*93*).

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Table II. Summary of greenhouse gas emissions from various composting studies

Compost material	*Method*	*CH_4 emissions*	*N_2O emissions*	*CO_2 emissions*	*Reference*
Beef manure	Windrow	0.742 g m^{-2} d^{-1}	NA	23.0 g m^{-2} d^{-1}	(*117*)
Beef manure + cattle mortality	Windrow	2.204 g m^{-2} d^{-1}	NA	53.6 g m^{-2} d^{-1}	(*117*)
Beef manure	Windrow	2.60 g m^{-2} d^{-1}	0.098 g m^{-2} d^{-1}	129.1 g m^{-2} d^{-1}	(*87*)
Beef manure DDGS diet	Windrow	2.42 g m^{-2} d^{-1}	0.213 g m^{-2} d^{-1}	115.6 g m^{-2} d^{-1}	(*87*)
Beef manure	Passive windrow	132.3 kg CO_2 eq. Mg^{-1}	34.1 kg CO_2 eq. Mg^{-1}	73.8 kg CO_2 eq. Mg^{-1}	(*32*)
Beef manure	Active windrow	170.1 kg CO_2 eq. Mg^{-1}	58.9 kg CO_2 eq. Mg^{-1}	168.0 kg CO_2 eq. Mg^{-1}	(*32*)
Beef manure	Windrow	322.6 kg CO_2 eq. Mg^{-1}	1.6 kg CO_2 eq. Mg^{-1}	93.7 kg CO_2 eq. Mg^{-1}	(*108*)
Beef manure + 30% phosphogypsum	Windrow	278.9 kg CO_2 eq. Mg^{-1}	1.95 kg CO_2 eq. Mg^{-1}	100.3 kg CO_2 eq. Mg^{-1}	(*108*)
Beef manure + mtraw + mattle mortality	Windrow	1.57 g $d^{-1}m^{-2}$	0.17 g $d^{-1}m^{-2}$	31.6 g $d^{-1}m^{-2}$	(*22*)
Beef manure + straw + SRM	Windrow	0.47 g $d^{-1}m^{-2}$	0.17 g $d^{-1}m^{-2}$	24.3 g $d^{-1}m^{-2}$	(*22*)
Beef manure	Windrow	0.053 kg Mg^{-1}	0.004 kg Mg^{-1}	10.8 kg Mg^{-1}	(*88*)
Beef manure + TYL11 antibiotic	Windrow	0.074 kg Mg^{-1}	0.032 kg Mg^{-1}	34.4 kg Mg^{-1}	(*88*)
Cattle and horse manure	Windrow	NA	0.5% of total N	NA	(*84*)
Swine manure + straw	Passive pile	0.2 % of total C	0.8 % of total N	8 % of total C	(*74*)
Swine manure + cardboard	In vessel	NA	0.1 % of total N	NA	(*85*)
Grass + green waste	In vessel	1.7 % of Total C	0.5 % of total N	81 % of total C	(*99*)

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Compost material	*Method*	*CH_4 emissions*	*N_2O emissions*	*CO_2 emissions*	*Reference*
Swine manure	Small pile in controlled chamber	1.0 g kg^{-1} OM	37.2 g kg^{-1} total N	NA	(*79*)
Swine manure	Large pile in controlled chamber	1.9 g kg^{-1} OM	46.5 g kg^{-1} total N	NA	(*79*)
Swine manure	Pile in controlled chamber	NA	88.5 g kg^{-1} total N	NA	(*114*)
Swine manure + NOB	Pile in controlled chamber	NA	20.2 g kg^{-1} total N	NA	(*114*)

Another strategy for limiting GHG emissions from compost piles is to modify the compost turning strategy. Compost turning introduces O_2 throughout the pile, restores pore space structure, and breaks up anaerobic zones. Compared to manure stockpiling, turning or forced aeration reduces CH_4 emissions significantly (*96*, *97*). However, turning also transfers some NO_2^- from the aerobic surface zones into the middle of the compost pile (*32*). In only 12 h after a turning event, the O_2 levels can fall below 3%, potentially fostering denitrification of NO_2^- and subsequent N_2O emissions (*32*). In a study comparing static pig manure compost piles, monthly turning resulted in ~4× less N_2O emission than with no turning (*90*). Similarly, the amount of organic C degradation resulting in CH_4 formation was only 0.5% in turned piles, compared with over 12% in unturned piles. Frequent compost turning, or even forced aeration, does not completely prevent the formation of anaerobic zones (*32*, *90*, *98–101*), so this strategy is only partially effective in mitigating GHG emissions. Frequent turning has also been reported to increase N-loss via NH_3 (*102*). In some circumstances, frequent compost turning may actually increase GHG emissions compared to unturned static piles (*32*). In that study, frequent turning reduced CH_4 concentration but almost doubled N_2O emissions (Table II). Compost turning also requires the use of heavy machinery, so GHG emissions due to fossil fuel use must also be considered in the overall GHG emission calculations (*33*, *91*). However, optimizing the composting process by balancing turning frequency with optimum water content and C/N ratio will shorten the time required to reach compost maturity and thus shorten the window of GHG emission during composting (*89*, *103*).

Bulking agents such as wood chips and straw can be incorporated into the compost mix to reduce bulk density and enhance O_2 diffusion into the compost pile, limiting the formation of anaerobic zones (*33*, *104*, *105*). Increasing pile density results in greater N_2O emissions (*106*). Inclusion of straw when composting pig or cattle manure results in reduced bulk density and reduced GHG emissions (*74*, *105*). Enhanced air circulation from straw inclusion reduces the development of anaerobic zones, but increased aeration can also enhance NH_3 emission (*107*). While this NH_3 loss reduces N_2O formation due to nitrification (*74*), it also lowers the N-content of the final compost product, reducing its value as a fertilizer (*32*). Kuroda et al. (*85*) found that little CH_4 was emitted when swine manure was composted in a mixture with cardboard in a lab scale active aeration system. However, some N_2O emission still occurred despite the maintenance of aerobic conditions, most likely due to oxidation of NH_3 to NO_2^- and subsequent conversion to N_2O. Moisture content also plays a role in the efficacy of O_2 diffusion within the compost pile. If there is too much water then pore spaces have less volume available for gas diffusion, increasing the likelihood of anaerobic zones forming.

Although pile turning and addition of bulking agents can reduce the prevalence of anaerobic zones, such strategies cannot completely prevent their formation in full scale compost windrows (*32*, *98*). A different strategy for reducing GHG emissions involves manipulation of the microbial community structure through the addition of amendments to the compost pile. One such amendment is phosphogypsum (PG; $CaSO_4{\cdot}2H_2O$), which is a byproduct of the phosphate fertilizer and construction industry (*108*). Addition of PG to compost

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

increases the S content while decreasing pH. Lower pH has been associated with increased N_2O emissions from soil (*109*). When added in sufficient quantities (20 or 30% by dry weight), PG reduces CH_4 emissions while having no effect on CO_2 or N_2O emissions (*108*). The reduction in CH_4 emission is likely due to the activity of sulphate reducing bacteria (SRB), which utilize sulphate as an electron acceptor and out-compete methanogens for nutrients (*37*, *110*). Additionally, a variety of sulphur compounds such as SO_4^{2-}, S^{2-}, and SO_3^{2-} adversely affect methanogen activity (*111*, *112*).

Another compost amendment of interest is the addition of nitrite oxidizing bacteria (NOB). The activities of ammonia oxidizing bacteria (AOB) lead to NO_2^- formation, while NOB activity prevents NO_2^- accumulation (Figure 2A). Under typical compost conditions, AOB produce NO_2^- at a greater rate than NOB can consume it, leading to NO_2^- accumulation. This is due to NOB having a slower growth rate (*113*) and their sensitivity to free NH_3 and nitrous acid (*81*). Since accumulated NO_2^- can yield N_2O through chemodenitrification or nitrifier denitrification (Figure 2B, C), supplementing the initial NOB population can reduce N_2O emission (*32*, *114*). If the total concentration of NOB can be increased to 10^6 cells g^{-1} compost, the activities of AOB and NOB can be balanced, reducing NO_2^- accumulation and in turn reducing N_2O emissions by up to 80% (*114*). Applying finished compost, which is rich in NOB, to mesophilic stage compost resulted in a 70% reduction in N_2O emission from swine manure in laboratory scale composters (*115*). Certain chemicals, which act as nitrification inhibitors that have been demonstrated to reduce N_2O emissions from soils by preventing NO_2^-, could potentially be applied to compost to suppress N_2O emissions (*70*).

Co-composting animal mortalities and SRM for control of infectious disease outbreaks has been investigated increasingly in recent years (*19*–*22*, *116*). From a GHG emission perspective, inclusion of animal tissues increases organic N levels and additionally favors the development of anaerobic zones within the compost pile due to poor aeration and accelerated microbial activity. In general, mortality composting results in greater GHG emissions than basic manure composting (*116*, *117*). Comparing GHG emissions from SRM vs. intact beef cattle carcasses, the latter emitted more CH_4 while CO_2 and N_2O levels did not significantly differ (*22*).

Composting, Soil C Sequestration, and Reduction in Chemical Inputs for Soil Fertility

Thus far the focus of the discussion has been on GHG emissions from active compost piles. Another important aspect to consider is the long term effect of composting on enhancing and maintaining agricultural soil fertility. As discussed previously, the majority of CO_2 emissions from compost occur during the active or thermophilic phase. Over time CO_2 emission decreases as organic matter degradation slows. Eventually the compost process is completed and the finished product can be applied to soils. Storage of finished compost does not significantly contribute to further GHG emissions, although it does increase the mineral N content which is advantageous from a fertilization perspective (*118*). Finished compost applied to soil will still slowly emit CO_2 as it is further degraded (*103*).

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Estimating the lifespan of soil organic C from compost applied to land is difficult based on the variability of many factors, such as soil type, temperature, and moisture, all of which affect the C turnover rate (*119*). However, it has been reported that 9% of organic C applied to soil as compost will remain after 100 years (*120*). This implies that sequestration of C in the soil is limited over a long time horizon, but application of compost derived organic C has many other GHG reduction benefits as well.

Application of compost to soil enhances soil fertility, stabilizes soil structure, enhances water holding capacity, and reduces the need for inputs such as chemical fertilizers and pesticides (*34*). Production of P_2O_5 fertilizer from rock phosphate requires approximately 243 kWh tonne^{-1} (*121*). Applying 10 tonnes of compost ha^{-1} would displace 190 kg of N fertilizer, providing an energy savings of 160-1590 kWh in fertilizer production costs alone. Over 20 years, the application of 10 tonnes compost ha^{-1} would offset 60-600 kg of CO_2 eq. N_2O compared to using chemical fertilizer. In addition to the above benefit, N_2O emissions from chemical fertilizers are greater than from compost amendment (*34*). Application of compost to soils has a negligible impact on overall GHG emissions from soil while improving soil N and C (*17*). In addition to nutrients and degradable substrates, compost application to soil also includes active microorganisms (*122*), which indirectly alter the microbial community composition of soil (*123*). Because the final compost product is relatively dry, odorless, and free of pathogens, transport and application to land a greater distance away from areas of intensive manure production is more economical, reducing the potential for excessive nutrient loading into water resources.

Anaerobic Digestion for Pretreatment of Manure

Anaerobic digestion (AD) is an engineered, tightly controlled process that takes advantage of the activities of anaerobic microbes to convert organic waste into CH_4 and CO_2 (Figure 1). Anaerobic digestion can be applied at a variety of temperature ranges, operating conditions, and using different reactor configurations, which will not be discussed here (*124*). Typically the ratio of CH_4 to CO_2 produced during AD is 2:1 (by % concentration). The yield of CH_4 from AD of manures ranges from 0.2-0.4 L CH_4/g VS for swine, 0.2-0.3 L CH_4/g VS for beef, and 0.3-0.35 L CH_4/g VS for poultry (*124*). Instead of being emitted to the atmosphere, the CH_4 produced is combusted for energy production. The net result of AD coupled with combustion of CH_4 is that only CO_2 and H_2O are emitted, making the process GHG neutral. This assumption is predicated on the fact that there are no fugitive CH_4 emissions from the AD reactor or the long-term effluent storage tank for treated manure (*124*). Although NH_4^+ is produced during AD, the absence of O_2 prevents nitrification (and subsequently denitrification), greatly decreasing the potential for N_2O formation during digestion (*12*).

One of the most desirable aspects of composting manure is that the final compost product is a good fertilizer and soil conditioner. The percentage of organic matter converted to gas during AD varies depending on the degradability of the substrate and the process conditions employed, but volatile solid degradation rates of over 50% are typical. The remaining organic matter consists primarily of components that are too difficult to degrade within the time frame of the AD process (typically days vs. months for composting). These remaining solids can either be collected and composted or directly applied to land as slurry, and used as fertilizer and soil conditioner. Some care must be taken when applying AD slurry, as it contains high levels of NH_4^+, which can be lost through volatilization if not injected into soil (*125*). Acidification of slurry may be a method to enhance stabilization of NH_4^+ and limit volatilization (*126*). Anaerobic digestion has additional benefits compared to land application of raw manure such as pathogen reduction, elimination of malodour, and prevention of nutrient leaching or runoff (*5*).

Slurry that has been processed by AD prior to land application may emit less N_2O than untreated slurry (*127–130*), but a significant reduction is not always observed, likely due to the complex nature of N_2O emission after land application (*124*). During storage anaerobically digested slurry produces 30-66% less CH_4 than non-digested slurry (*128*, *131*). In a dairy manure system, implementing AD instead of slurry storage could result in CH_4 reduction of ~300 kg CO_2 eq. per livestock unit (*132*). The same authors found that implementing AD in that system would enhance N_2O emissions after field application, but that the reduced need for additional N-requirements helped offset this disadvantage. Solids that are subjected to AD and then composted emit significantly less GHGs when compared to composting raw solids (*133*).

In a study comparing GHG emissions from beef or dairy manure that was either stockpiled, stored as slurry, or composted, compost was found to produce the lowest CH_4 emissions but the highest N_2O (*10*). While the pattern was the same for both beef and dairy manure, CH_4 and N_2O emissions from dairy manure were higher than for beef. Comparisons of total GHG estimates revealed that compost produced the lowest emissions, followed by manure stockpiling, and finally slurry storage. Taking into account subsequent land application of the composted or stored manure, the emission hierarchy remained the same. If applied to Canada, switching all slurry and manure stockpiling to composting would result in a GHG reduction of 0.7 Tg CO_2 eq. In contrast, if all manure was stored as slurry and then processed by AD, a 1.08 Tg CO_2 eq. reduction in GHG would be possible.

Summary

Composting livestock manures offers a management strategy with advantages and disadvantages. The cost of GHG and ammonia emissions must be balanced against the other environmental and economic benefits, such as increased soil fertility and structure, reduced reliance on chemical fertilizers, and control of odors and nutrient displacement. Composting within enclosed facilities, potentially enabling recapture or removal of fugitive GHG and ammonia emissions, could further enhance the benefits of composting. Where feasible, anaerobic digestion can be used in place of, or in conjunction with, composting to maximize the benefits of nutrient recycling via manure management while reducing GHG emissions.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

References

1. IPCC (Intergovernmental Panel on Climate Change). *The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, U.K., 2001.
2. WHO (World Health Organization). *Global and Regional Food Consumption Patterns and Trends*; 2008, URL http://who.int/nutrition/topics/3_foodconsumption/en/index4.html.
3. Oenema, O.; Wrage, N.; Velthof, G. L.; van Groenigen, J. W.; Dolfing, J.; Kuikman, P. J. *Nutr. Cycling. Agroecosyst.* **2005**, *72*, 51–65.
4. Davidson, E. A. *Nat. Geosci.* **2009**, *2*, 659–662.
5. Steinfeld, H.; Gerber, P.; Wassenaar, T.; Castel, V.; Rosales, M.; De Haan, C. In *Food and Agriculture Organization of the United Nations: Livestock's Long Shadow: Environmental Issues and Options*; 2006, URL http://www.fao.org/docrep/010/a0701e/a0701e00.htm.
6. Svensson, B. H.; Lantsheer, J. C.; Rodhe, H. *Ambio* **1991**, *20*, 155–160.
7. Khalil, M. A. K.; Rasmussen, R. A. *J. Geophys. Res., [Atmos.]* **1992**, *97*, 14651–14660.
8. Sommer, S. G.; Petersen, S. O.; Sogaard, H. T. *J. Environ. Qual.* **2000**, *29*, 744–751.
9. Kulling, D. R.; Dohme, F.; Menzi, H.; Sutter, F.; Lischer, P.; Kreuzer, M. *Environ. Monit. Assess.* **2002**, *79*, 129–150.
10. Pattey, E.; Trzcinski, M. K.; Desjardins, R. L. *Nutr. Cycling Agroecosyst.* **2005**, *72*, 173–187.
11. Mosier, A.; Kroeze, C.; Nevison, C.; Oenema, O.; Seitzinger, S.; van Cleemput, O. *Nutr. Cycling Agroecosyst.* **1998**, *52*, 225–248.
12. Chadwick, D.; Sommer, S.; Thorman, R.; Fangueiro, D.; Cardenas, L.; Amon, B.; Misselbrook, T. *Anim. Feed Sci. Technol.* **2011**in press.
13. IPCC (Intergovernmental Panel on Climate Change). *The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, U.K., 2007.
14. Cicerone, R. J. *Science* **1987**, *237*, 35–42.
15. Cicerone, R. J.; Oremland, R. S. *Global Biogeochem. Cycles* **1988**, *2*, 299–327.
16. Hellmann, B.; Zelles, L.; Palojarvi, A.; Bai, Q. Y. *Appl. Environ. Microbiol.* **1997**, *63*, 1011–1018.
17. Ginting, D.; Kessavalou, A.; Eghball, B.; Doran, J. W. *J. Environ. Qual.* **2003**, *32*, 23–32.
18. Kebreab, E.; Clark, K.; Wagner-Riddle, C.; France, J. *Can. J. Anim. Sci.* **2006**, *86*, 135–158.
19. Stanford, K.; Larney, F. J.; Olson, A. F.; Yanke, L. J; McKenzie, R. H. *Compost Sci. Util.* **2000**, *8*, 135–146.
20. Kalbasi, A.; Mukhtar, S.; Hawkins, S. E.; Auvermann, B. W. *Compost Sci. Util.* **2005**, *13*, 180–193.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

21. Xu, W. P.; Xu, Y. P.; Reuter, T.; Gilroyed, B.; Jin, L.; Stanford, K.; Larney, F. J.; McAllister, T. A. *Compost Sci. Util.* **2010**, *18*, 32–41.
22. Hao, X.; Stanford, K.; McAllister, T. A.; Larney, F. J.; Xu, S. W. *Nutr. Cycling Agroecosyst.* **2009**, *83*, 289–299.
23. Gilroyed, B. H.; Reuter, T.; Chu, A.; Hao, X.; Xu, W. P.; McAllister, T. A. *Bioresour. Technol.* **2010**, *101*, 5780–5785.
24. Gilroyed, B. H.; Li, C. L.; Hao, X.; Chu, A.; McAllister, T. A. *Int. J. Hydrogen Energy* **2010**, *35*, 1099–1105.
25. Larney, F. J.; Sullivan, D. M.; Buckley, K. E.; Eghball, B. *Can. J. Soil Sci.* **2006**, *86*, 597–611.
26. Larney, F. J.; Hao, X. *Bioresour. Technol.* **2007**, *98*, 3221–3227.
27. Larney, F. J.; Olson, A. F.; Cárcamo, H. A.; Chang, C. *Bioresour. Technol.* **2000**, *75*, 139–148.
28. Larney, F. J.; Yanke, L. J.; Miller, J. J.; McAllister, T. A. *J. Environ. Qual.* **2003**, *32*, 1508–1515.
29. Van Herk, F. H.; McAllister, T. A.; Cockwill, C. L.; Guselle, N.; Larney, F. J.; Miller, J. J.; Olson, M. E. *Compost Sci. Util.* **2004**, *12*, 235–241.
30. Larney, F. J.; Turkington, T. K. *Compost Sci. Util.* **2009**, *17*, 247–256.
31. Larney, F. J.; Blackshaw, R. E. *J. Environ. Qual.* **2003**, *32*, 1105–1113.
32. Hao, X.; Chang, C.; Larney, F . J.; Travis, G. R. *J. Environ. Qual.* **2001**, *30*, 376–386.
33. Hao, X.; Chang, C.; Larney, F. J. *J. Environ. Qual.* **2004**, *33*, 37–44.
34. Favoino, E.; Hogg, D. The potential role of compost in reducing greenhouse gases. *Waste Manage. Res.* **2008**, *26*, 61–69.
35. Ferry, J. G. *Planet. Space Sci.* **2010**, *58*, 1775–1783.
36. Gottschalk, G. *Bacterial Metabolism*; Springer-Verlag New York Inc.: New York, 1986.
37. Thauer, R. K.; Kaster, A. K.; Seedorf, H.; Buckel, W.; Hedderich, R. *Nature Rev. Microbiol.* **2008**, *6*, 579–591.
38. Jang, H. D.; Yang, S. S. *J. Biomass Energ. Soc. China* **2001**.
39. Chae, K. J.; Choi, M. J.; Kim, K. Y.; Ajayi, F. F.; Chang, I. S.; Kim, I. S. *Int. J. Hydrogen Energy* **2010**, *35*, 13379–13386.
40. Oh, S. E.; Van Ginkel, S.; Logan, B. E. *Environ. Sci. Technol.* **2003**, *37*, 5186–5190.
41. Dhaked, R. K.; Singh, P.; Singh, L. *Waste Manage.* **2010**, *30*, 2490–2496.
42. Lee, M.; Hidaka, T.; Hagiwara, W.; Tsuno, H. *Bioresour. Technol.* **2009**, *100*, 578–585.
43. Dumont, M. G.; Murrell, J. C. *Community-Level Analysis: Key Genes of Aerobic Methane Oxidation*; Elsevier Academic Press Inc.: San Diego, CA, 2005.
44. Hakemian, A. S.; Rosenzweig, A. C. *Annu. Rev. Biochem.* **2007**, *76*, 223–241.
45. Halet, D.; Boon, N.; Verstraete, W. *J. Biosci. Bioeng.* **2006**, *101*, 297–302.
46. Seghers, D.; Verthe, K.; Reheul, D.; Bulcke, R.; Siciliano, S. D.; Verstraete, W.; Top, E. M. *FEMS Microbiol. Ecol.* **2003**, *46*, 139–146.
47. Seghers, D.; Top, E. M.; Reheul, D.; Bulcke, R.; Boeckx, P.; Verstraete, W.; Siciliano, S. D. *Environ. Microbiol.* **2003**, *5*, 867–877.

48. Amaral, J. A.; Knowles, R. *FEMS Microbiol. Lett.* **1995**, *126*, 215–220.

49. Henckel, T.; Roslev, P.; Conrad, R. *Environ. Microbiol.* **2000**, *2*, 666–679.

50. Zhang, Y.; Henriet, J. P.; Bursens, J.; Boon, N. *Bioresour. Technol.* **2010**, *101*, 3132–3138.

51. Jackel, U.; Thummes, K.; Kampfer, P. *FEMS Microbiol. Ecol.* **2005**, *52*, 175–184.

52. Wrage, N.; Velthof, G. L.; van Beusichem, M. L.; Oenema, O. *Soil Biol. Biochem.* **2001**, *33*, 1723–1732.

53. Leininger, S.; Urich, T.; Schloter, M.; Schwark, L.; Qi, J.; Nicol, G. W.; Prosser, J. I.; Schuster, S. C.; Schleper, C. *Nature* **2006**, *442*, 806–809.

54. Martens-Habbena, W.; Berube, P. M.; Urakawa, H.; de la Torre, J. R.; Stahl, D. A. *Nature* **2009**, *461*, 976–979.

55. Yamamoto, N.; Otawa, K.; Nakai, Y. *Microbial Ecol.* **2010**, *60*, 807–815.

56. van Cleemput, O.; Baert, L. *Plant Soil* **1984**, *76*, 233–241.

57. Otte, S.; Schalk, J.; Kuenen, J. G.; Jetten, M. S. M. *Appl. Microbiol. Biotechnol.* **1999**, *51*, 255–261.

58. Hooper, A. B.; Terry, K. R. *Biochim. Biophys. Acta* **1979**, *571*, 12–20.

59. Schlegel, H. G. *Allgemeine Mikrobiologie*, 7th ed; Thieme Verlag: Suttgart, NY, 1992.

60. Robertson, L. A.; Cornelisse, R.; Devos, P.; Hadioetomo, R.; Kuenen, J. G. *Antonie Van Leeuwenhoek J. Microbiol.* **1989**, *56*, 289–299.

61. Papen, H.; Vonberg, R.; Hinkel, I.; Thoene, B.; Rennenberg, H. *Appl. Environ. Microbiol.* **1989**, *55*, 2068–2072.

62. Anderson, I. C.; Poth, M.; Homstead, J.; Burdige, D. *Appl. Environ. Microbiol.* **1993**, *59*, 3525–3533.

63. Firestone, M. K. In *Nitrogen in agricultural soils*; Stevenson, F. J., Ed.; Agronomy **1982**, 22, 289−326.

64. Morozkina, E. V.; Kurakov, A. V. *Appl. Biochem. Microbiol.* **2007**, *43*, 544–549.

65. Knowles, R. *Microbiol. Rev.* **1982**, *46*, 43–70.

66. Khdyer, I. I.; Cho, C. M. *Soil Sci. Soc. Am. J.* **1983**, *47*, 1134–1139.

67. Kuai, L. P.; Verstraete, W. *Appl. Environ. Microbiol.* **1998**, *64*, 4500–4506.

68. Robertson, G. P.; Tiedje, J. M. *Soil Biol. Biochem.* **1987**, *19*, 187–193.

69. Webster, E. A.; Hopkins, D. W. *Biol. Fertil. Soils* **1996**, *22*, 326–330.

70. Maeda, K.; Toyoda, S.; Shimojima, R.; Osada, T.; Hanajima, D.; Morioka, R.; Yoshida, N. *Appl. Environ. Microbiol.* **2010**, *76*, 1555–1562.

71. Paillat, J. M.; Robin, P.; Hassouna, M.; Leterme, P. *Atmos. Environ.* **2005**, *39*, 6833–6842.

72. Novinscak, A.; DeCoste, N. J.; Surette, C.; Filion, M. *Can. J. Microbiol.* **2009**, *55*, 375–387.

73. Partanen, P.; Hultman, J.; Paulin, L.; Auvinen, P.; Romantschuk, M. *BMC Microbiol.* 2010, doi:10.1186/1471-2180-10-94.

74. Sommer, S. G.; Møller, H. B. *J. Agric. Sci.* **2000**, *134*, 327–335.

75. Sommer, S. G.; Mcginn, S. M.; Hao, X.; Larney, F. J. *Atmos. Environ.* **2004**, *38*, 4643–4652.

76. Fukumoto, Y.; Rom, H. B.; Dahl, P. *J. Sci. Res. Dev.* 2003, Manuscript EE 03 004.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

77. Sharma, R.; Ryan, K.; Hao, X.; Larney, F. J.; McAllister, T. A.; Topp, E. *J. Environ. Qual.* **2011**, *40*, 199–205.
78. Martins, O.; Dewes, T. *Bioresour. Technol.* **1992**, *42*, 103–111.
79. Fukumoto, Y.; Osada, T.; Hanajima, D.; Haga, K. *Bioresour. Technol.* **2003**, *89*, 109–114.
80. Zeman, C.; Depken, D.; Rich, M. *Compost Sci. Util.* **2002**, *10*, 72–86.
81. Anthonisen, A. C.; Loehr, R. C.; Prakasam, T. B. S.; Srinath, E. G. *J. - Water Pollut. Control Fed.* **1976**, *48*, 835–852.
82. Shimaya, C.; Hashimoto, T. *Soil Sci. Plant Nutr.* **2008**, *54*, 529–533.
83. Jarvis, A.; Sundberg, C.; Milenkovski, S.; Pell, M.; Smars, S.; Lindgren, P. E.; Hallin, S. *J. Appl. Microbiol.* **2009**, *106*, 1502–1511.
84. Czepiel, P.; Douglas, E.; Harriss, R.; Crill, P. *Environ. Sci. Technol.* **1996**, *30*, 2519–2525.
85. Kuroda, K.; Osada, T.; Yonaga, M.; Kanematu, A.; Nitta, T.; Mouri, S.; Kojima, T. *Bioresour. Technol.* **1996**, *56*, 265–271.
86. He, Y. W.; Inamori, Y.; Mizuochi, M.; Kong, H. N.; Iwami, N.; Sun, T. H. *Sci. Total Environ.* **2000**, *254*, 65–74.
87. Hao, X.; Xu, S.; Larney, F. J.; Stanford, K.; Cessna, A. J.; McAllister, T. A. *Nutr. Cycling Agroecosyst.* **2011**, *89*, 257–267.
88. Hao, X.; Benke, M.; Larney, F. J.; McAllister, T. A. *Nutr. Cycling Agroecosyst.* **2011**, *89*, 105–114.
89. Chang, C. H.; Chen, I. C.; Yang, S. S. *Terr. Atmos. Ocean. Sci.* **2009**, *20*, 511–520.
90. Szanto, G. L.; Hamelers, H. M.; Rulkens, W. H.; Veeken, A. H. M. *Bioresour. Technol.* **2007**, *98*, 2659–2670.
91. Boldrin, A.; Andersen, J. K.; Moller, J.; Christensen, T. H.; Favoino, E. *Waste Manage. Res.* **2009**, *27*, 800–812.
92. Schattner-Schmidt, S.; Helm, M.; Gronauer, A.; Hellmann, B. *Landtechnik* **1995**, *50*, 364.
93. Beck-Friis, B.; Pell, M.; Sonesson, U.; Jonsson, H.; Kirchmann, H. *Environ. Monit. Assess.* **2000**, *62*, 317–331.
94. Haga, K. *Jarq-Jpn. Agr. Res. Q.* **1998**, *32*, 203–210.
95. Ashbolt, N. J.; Line, M. A. *J. Environ. Qual.* **1982**, *11*, 405–408.
96. LopezReal, J.; Baptista, M. *Compost Sci. Util.* **1996**, *4*, 71–82.
97. Park, K. H.; Jeon, J. H.; Jeon, K. H.; Kwag, J. H.; Choi, D. Y. *Anim. Feed Sci. Technol.* **2011**in press.
98. Atkinson, C. F.; Jones, D. D.; Gauthier, J. J. *J. Ind. Microbiol.* **1996**, *16*, 182–188.
99. Hellebrand, H. J. *J. Agric. Eng. Res.* **1998**, *69*, 365–375.
100. Thompson, A. G.; Wagner-Riddle, C.; Fleming, R. *Environ. Monit. Assess.* **2004**, *91*, 87–104.
101. Hobson, A. M.; Frederickson, J.; Dise, N. B. *Waste Manage.* **2005**, *25*, 345–352.
102. Amon, B.; Amon, T.; Boxberger, J.; Alt, C. *Nutr. Cycling Agroecosyst.* **2001**, *60*, 103–113.
103. Shi, W.; Norton, J. M.; Miller, B. E.; Pace, M. G. *Appl. Soil Ecol.* **1999**, *11*, 17–28.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

104. Mahimairaja, S.; Bolan, N. S.; Hedley, M. J. *Soil Biol. Biochem.* **1995**, *27*, 1223–1225.

105. Yamulki, S. *Agric. Ecosys. Environ.* **2006**, *112*, 140–145.

106. Webb, J.; Sommer, S. G.; Kupper, T.; Groenestein, K.; Huthings, N. J.; Eurich-Menden, B.; Rodhe, L.; Misselbrook, T. M.; Amon, B. *Sustainable. Agric. Rev.* **2011**, *8*in press.

107. Osada, T.; Kuroda, K.; Yonaga, M. *J. Mater. Cycles Waste Manage.* **2000**, *2*, 51–56.

108. Hao, X.; Larney, F. J.; Chang, C.; Travis, G. R.; Nichol, C. K.; Bremer, E. *J. Environ. Qual.* **2005**, *34*, 774–781.

109. Stevens, R. J.; Laughlin, R. J.; Malone, J. P. *Soil Biol. Biochem.* **1998**, *30*, 1119–1126.

110. Lovely, D. R.; Klug, M. J. *Appl. Environ. Microbiol.* **1983**, *45*, 187–192.

111. Lin, C. Y.; Chang, F. Y.; Chang, C. H. *J. Hazard. Mater.* **2001**, *87*, 11–21.

112. Pender, S.; Toomey, M.; Carton, M.; Eardly, D.; Patching, J. W.; Colleran, E.; O'Flaherty, V. *Water Res.* **2004**, *38*, 619–630.

113. Morrill, L. G.; Dawson, J. E. *Soil Sci. Soc. Am. J.* **1967**, *31*, 757–760.

114. Fukumoto, Y.; Suzuki, K.; Osada, T.; Kuroda, K.; Hanajima, D.; Yasuda, T.; Haga, K. *Environ. Sci. Technol.* **2006**, *40*, 6787–6791.

115. Fukumoto, Y.; Inubushi, K. *Soil Sci. Plant Nutr.* **2009**, *55*, 428–434.

116. Xu, S.; Hao, X.; Stanford, K.; McAllister, T. A.; Larney, F. J.; Wang, J. *J. Environ. Qual.* **2007**, *36*, 1914–1919.

117. Xu, S. W.; Hao, X.; Stanford, K.; McAllister, T.; Larney, F. J.; Wang, J. G. *Nutr. Cycling Agroecosyst.* **2007**, *78*, 177–187.

118. Hao, X. *Nutr. Cycling Agroecosyst.* **2007**, *78*, 189–195.

119. Smith, A.; Brown, K.; Ogilvie, S.; Rushton, K.; Bates, J. *Waste Management Options and Climate Change*; Final report to EC, DG ENV, AEA Technology, 2001.

120. Smith, P.; Powlson, D. S.; Glendining, M. J.; Smith, J. U. *Global Change Biol.* **1997**, *3*, 67–79.

121. UNEP and UNIDO (United Nations Environment Programme and United Nations Industrial Development Organisation). *Mineral Fertilizer Production and the Environment- Part 1: The Fertilizer Industry's Manufacturing Processes and Environmental Issues*; In collaboration with the International Fertilizer Industry Association Technical Report Number 26- Part 1; UNEP and UNIDO: Paris and Vienna, 1998.

122. Ryckeboer, J.; Mergaert, J.; Vaes, K.; Klammer, S.; De Clercq, D.; Coosemans, J.; Insam, H.; Swings, J. *Ann. Microbiol.* **2003**, *53*, 349–410.

123. Innerebner, G.; Knapp, B.; Vasara, T.; Romantschuk, M.; Insam, H. *Soil Biol. Biochem.* **2006**, *38*, 1092–1100.

124. Massé, D. I.; Talbot, G.; Gilbert, Y. *Anim. Feed Sci. Technol.*in press.

125. Jarvis, S. C.; Pain, B. F. *Gaseous Nitrogen Emissions from Grasslands*; CAB International: Wallingford, U.K., 1997.

126. Kai, P.; Pedersen, P.; Jensen, J. E.; Hansen, M. N.; Sommer, S. G. *Eur. J. Agron.* **2008**, *28*, 148–154.

127. Petersen, S. O. *J. Environ. Qual.* **1999**, *28*, 1610–1618.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

128. Amon, B.; Kryvoruchko, V.; Amon, T.; Zechmeister-Boltenstern, S. *Agric., Ecosyst. Environ.* **2006**, *112*, 153–162.
129. Chantigny, M. H.; Angers, D. A.; Rochette, P.; Belanger, G.; Masse, D.; Cote, D. *J. Environ. Qual.* **2007**, *36*, 1864–1872.
130. Chiyoka, W.; Hao, X.; Zvomuya, F.; Li, X. *Anim. Feed Sci. Technol.* **2011**in press.
131. Clemens, J.; Trimborn, M.; Weiland, P.; Amon, B. *Agric., Ecosyst. Environ.* **2006**, *112*, 171–177.
132. Petersen, S. O.; Sommer, S. G. *Anim. Feed Sci. Technol.* **2011** in press.
133. Edelmann, W.; Schleiss, K.; Joss, A. *Water Sci. Technol.* **2000**, *41*, 263–273.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch022

Chapter 23

Mitigation of Greenhouse Gas Emissions from U.S. Beef and Dairy Production Systems

**Sara E. Place, Kim R. Stackhouse, Qian Wang,
and Frank M. Mitloehner***

**Department of Animal Science, University of California, Davis,
2151 Meyer Hall, One Shields Avenue, Davis, CA 95616
*E-mail: fmmitloehner@ucdavis.edu**

Recently, there has been great interest regarding the contribution of the U.S. cattle industries (both beef production and dairy production systems) to anthropogenic climate change. As a result, research into greenhouse gas mitigation from these industries has been at the forefront in recent years. The sources of greenhouse gases from the cattle industry are complex, but can be placed into two categories: enteric and manure-derived emissions. This chapter will briefly introduce how greenhouse gases are produced from these sources and then provide an overview of the mitigation techniques, some of which are currently in use and others that are in the early stages of development and understanding.

Introduction

In the United States, the beef and dairy industries provide numerous high quality foodstuffs and byproducts for human use that have important economic and societal value. During the production of these valued goods, undesirable greenhouse gas (GHG) emissions can occur. The U.S. cattle industries are a significant source of the GHGs methane (CH_4) and nitrous oxide (N_2O), while carbon dioxide (CO_2) emissions from the production of beef and dairy products are a relatively minor contributor to the total U.S. GHG inventory. Mitigation of CH_4 from enteric fermentation processes in cattle has historically been investigated solely as a way to increase the nutritive value of feedstuffs; however, in recent decades, growing concern regarding anthropogenically-driven

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

climate change has spurred new interest in reducing CH_4 emissions from cattle. In cattle production, N_2O mainly occurs from cropland soils used to grow animal feedstuffs and long-term manure storage lagoons. While GHGs from manure are an adverse side effect of cattle production, the waste can be converted into valuable and environmentally sustainable products (e.g., treating the waste in anaerobic digesters to produce biogas for electricity generation). Quantifying and mitigating GHG from U.S. cattle production systems is challenging due to the variation across farms, ranches, and feedlots, and the variability within each system due to animal, management, and seasonal variations. Similarly, output per animal (e.g., kg of milk produced per dairy cow) across all U.S. beef and dairy systems is not uniform; therefore, mitigation options discussed throughout the chapter will be evaluated on their ability to reduce GHG per unit of output (e.g., per kg of energy-corrected milk or per kg of carcass weight) instead of per head of cattle.

Sources of Greenhouse Gases from U.S. Beef and Dairy Production

When discussing the mitigation of GHG from the production of beef and dairy products, the scope and boundaries of the analysis should be clearly defined. The broadest analysis would be a complete Life Cycle Assessment (LCA) of GHG emissions. A complete LCA of beef and dairy production would examine GHG emissions from the production of feedstuffs, the cattle, their waste, the on-farm electricity and fossil fuel use, the transportation and processing of products, and the retail and consumer levels. Such an exhaustive analysis is beyond the scope of a single chapter. Instead, this chapter will focus on the GHG emissions produced by the cattle directly and their waste and the mitigation options that exist to reduce GHG emissions from these segments. Additionally, as CO_2 emissions from the animals and their waste are considered carbon neutral (*1*), the GHG mitigation discussion will be limited to methane and N_2O emissions.

Methane

Methane is a GHG with a 100-year global warming potential (GWP) of 21 (*2*). In U.S. beef and dairy production, most CH_4 originates from the animal's digestive tract or from anaerobic manure storage systems. Cattle have a large specialized stomach composed of four compartments: the reticulum, the rumen, the omasum, and the abomasum. Of the four compartments, only the abomasum resembles the acidic stomach possessed by monogastrics, such as humans and pigs. When mature cattle ingest feed, it enters the reticulum and rumen first (sometimes referred to as the reticulorumen because of the constant interchange of contents between the two compartments), then passes to the omasum, and finally enters the abomasum. The rumen is by far the largest compartment (its volume can be up to 150 liters in mature dairy cows) and is of particular interest due to the methanogenic (methane-forming) microorganisms that can reside within this large fermentation vat. The rumen is home to a diverse array of billions of microorganisms including both prokaryotes (bacteria and archaea) and eukaryotes (protozoa and fungi). These organisms range from facultatively anaerobic to strictly anaerobic. The methane-forming methanogens, who belong to the archaea domain, are of the later group. As a result, CH_4 emissions resulting from beef and dairy production systems are limited to the anaerobic environment of the rumen and manure storage systems that are devoid of oxygen. Fresh waste from cattle and manure that is surface-applied to soil are not significant sources of CH_4.

Nitrous Oxide

Nitrous oxide is highly potent GHG with a 100-year GWP of 310; therefore, reducing N_2O emissions can have a significant impact on the overall GHG emissions from the U.S. beef and dairy production systems (*2*). Nitrous oxide is formed through anaerobic microbial processes during denitrification of nitrate (NO_3^-) to dinitrogen (N_2) gas. The major sources of N_2O from beef and dairy production are long-term manure storage lagoons and emissions from cropland fertilized with nitrogen fertilizer or manure (*3*, *4*). Small amounts of N_2O can result from nitrate reduction processes in the rumen (*5*); although, emissions of N_2O directly from cattle are not usually considered in analyses of GHG emissions (*6*) due to the lack of research that has quantified of *in vivo* emissions from beef and dairy cattle.

Mitigation of Greenhouse Gases from U.S. Beef and Dairy Production

Overview of Beef and Dairy Production in the United States

In the U.S. beef system, the majority of animals begin their lives on cow-calf operations, where British and Continental breeds of cows (typical breeds are e.g., Aberdeen-Angus and Simmental, respectively) are bred, give birth to calves, and nurse and graze with those calves on extensive rangelands or pastures until the calves are approximately five to seven months of age. After the calves are weaned (no longer allowed to nurse milk from their mothers), they either directly enter a feedlot (outdoor drylot corrals) or are further grazed on rangeland or pasture to a weight of approximately 350 to 400 kg before entering a feedlot. The path that a single calf takes to the feedlot greatly depends on the region and current economic conditions. Only a small specialty portion of U.S. beef cattle spends their entire lives on pastures or rangeland. Additionally, many of the male dairy calves in the Western U.S. are raised by a specialized segment of calf ranches until approximately 150 kg, at which time these calves will enter a feedlot.

The time an individual animal spends in a feedlot depends on its entering weight, its rate of weight gain, and the desired weight at harvest. Typically, U.S. beef cattle are on feed (in the feedlot) for 120 to 180 days. The diet the cattle are fed during this time is usually 75 to 90% concentrate (e.g., steam flaked corn grain, soybean meal, distiller’s grains (a byproduct of alcoholic beverage and ethanol for biofuels distillation), etc.) and 10 to 25% forage (e.g., grass or legume hay). As of July 2010, there were 87.6 million beef cattle in the U.S., which included 31.7 million beef cows and 12 million cattle in feedlots during that month (*7*).

The U.S. dairy industry also includes some exclusively extensive (grazing-based) operations, but a majority of dairies use confinement systems where animals are housed within a barn or corral area. The dairy industry has been steadily consolidating to fewer operations with a greater number of dairy cows per operation. In 2010, there were 9.1 million lactating dairy cows in the U.S., the majority of which are of the Holstein-Friesian breed (*7*). Since the U.S. Department of Agriculture (USDA) has recorded the national inventory of dairy cattle, the largest U.S. dairy herd was in 1944 with 25.6 million cows; however, today's herd produces 32.9 billion kg more milk per year with 16.4 million fewer cows (*8*), which has translated into significant reductions in the industry's environmental impact per unit of production (*9*).

The diets fed to dairy cattle in confinement systems varies from farm-to-farm depending on the crops that can be grown and purchased by the farm, but lactating dairy cow diets are typically at least 50% forage (corn silage, alfalfa hay or silage, grass hay or silage, etc.) and 50% concentrate (corn grain, high moisture shell corn, soybean meal, etc.). Depending on their price and availability, byproducts, such as cottonseed, almond hulls, and citrus pulp, are often included in the diets of dairy cows.

In summary, much variation exists across and within individual dairy and beef production units (farms, ranches, and feedlots) in terms of management, nutrition, and animal types. The following discussion of mitigation will focus first on the strategies to directly reduce CH_4 from the rumen (enteric fermentation), then how production efficiency can reduce GHG, and finally a discussion of mitigating manure-derived GHG emissions.

Mitigation of Enteric Emissions through Dietary Strategies

The diet that is fed to cattle greatly determines the CH_4 emissions that will be eructated by the animal. Figure 1 is a simplified representation of the fermentative processes that occur within the rumen of beef and dairy cattle. The microbes in the rumen ferment carbohydrates and proteins to short-chain fatty acids, known as volatile fatty acids (VFA), and ammonia. The three most prevalent VFA in the rumen of cattle are acetate, propionate, and butyrate. These VFA are absorbed through the rumen epithelium, and are used by the animal as sources of energy. Of the three VFA, only the three-carbon propionate can be used as a substrate for glucose production (aka gluconeogenesis), which is critical for efficient growth and milk production, while acetate and butyrate are primarily used for the production of fat or oxidized for energy. When acetate and butyrate are the fermentation end products, there is a net production of hydrogen gas (H_2). If H_2 accumulates in the rumen, it can inhibit microbial enzymes that are critical for fermentation to occur, which causes the rumen digestibility of feedstuffs to decline (*10*). However, in a normally functioning rumen, the H_2 concentration is kept very low by the methanogens that use H_2 to reduce CO_2 to CH_4 (i.e., methanogenesis) (*11*). This process serves as the main energy-producing pathway for the methanogens, who are often found in close association with rumen protozoa that produce H_2 (*12*, *13*).

The total amount of CH_4 produced from an individual cow or steer largely depends on the population size and turnover of methangens and the amount of H_2 that is available for methanogenesis. Therefore, mitigating CH_4 produced in the rumen of cattle requires the manipulation of these factors. The following sections will briefly cover the major known ways to mitigate enteric CH_4.

Type of Dietary Carbohydrates

Not all carbohydrates included in the diet of cattle undergo the same microbial fermentation processes, which leads to differences in the relative amounts of acetate, propionate, and butyrate produced. It has been long established that diets higher in fiber (the structural carbohydrates of the plant, including cellulose and hemicellulose) lead to increased acetate production, and, consequently, increased CH_4 production from the cow (*13*). The quality of the forages (e.g., the maturity of the plant at harvest, the quality of the preservation process, etc.) offered to cattle will greatly determine the actual CH_4 emissions produced per unit of feed intake, because of disparities in digestibility and rate-of-passage (*13*). Diets high in non-structural carbohydrates (e.g., starch), such as the high concentrate diets fed to beef cattle in feedlots, typically yield less CH_4 per unit of dry matter intake compared to high fiber diets.

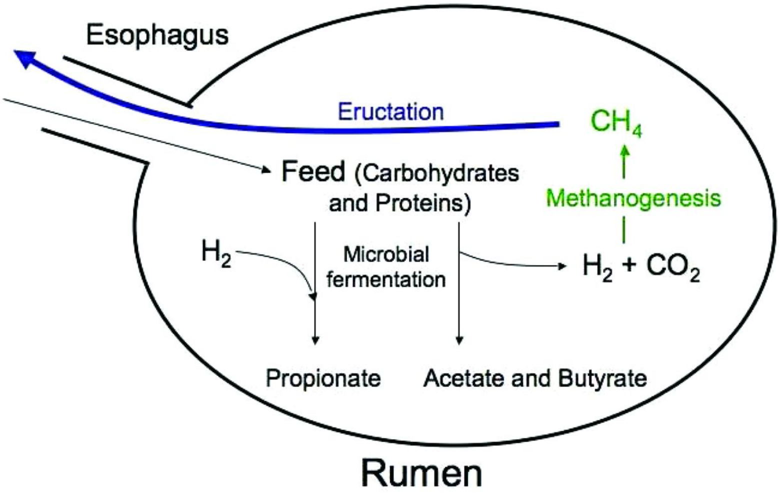


Figure 1. Simplified model of rumen fermentation.

However, simply feeding higher concentrate diets (75 to 90% of diet) to all beef and dairy cattle in the U.S. is not a realistic solution. First, the cost of feeding cattle high concentrate diets is much greater than the extensive pasture and rangeland systems under which the majority of U.S. beef cows and calves are currently raised. Additionally, very high concentrate diets carry the risk of the animal developing rumen acidosis, which can make the animal ill or lead to death (*14*). In dairy production systems, where ideally a single dairy cow will live at least four or more years, this risk of acidosis is too costly. Furthermore, high concentrate diets have been linked to milk fat depression in dairy cattle, an undesirable condition that dairy producers try to avoid (*15*). Finally, while beyond the scope of this chapter, the contribution of growing grains to whole farm GHG emissions should be considered as well. However, properly balanced, cost-effective diets for both feedlot cattle and dairy cattle that utilize more fermentable carbohydrates are currently in use in the U.S. and have resulted in undoubtedly lower enteric CH_4 emissions compared to exclusively extensive beef and dairy systems.

Ionophores

One class of feed additives currently in widespread use in both the beef and dairy industries are ionophores. Ionophores are a class of anti-microbials that transport ions across cell membranes, thereby disrupting chemi-osmotic gradients. These disruptions often lead to a decrease in ATP-production efficiency by the affected microbial cell (*16*). Historically, these ionophores have been used for disease prevention, specifically to prevent coccidiosis (*17*). However, it was found that one of these ionophores, monensin, had the potential to increase feed efficiency (decrease the amount of feed required to produce a kg of bodyweight gain) and reduce the incidence of rumen acidosis in cattle, which lead to its more widespread use and the search for similar compounds that could have comparable effects. Other ionophores approved for animal use, but used to a lesser extent than monensin, include laidlomycin, lasalocid, and narasin (*18*). The improvement in feed efficiency is attributed to a shift in rumen fermentation that leads to more propionate production relative to acetate production and a decrease in methanogenesis, which together translate into a more efficient conversion of dietary gross energy into net energy that the animal can use for its maintenance and production needs (*19*).

Some of the research on monensin has shown conflicting results in regard to the compound's ability to reduce CH_4 emissions, or shown only short-term decreases of CH_4 (on the time-scale of two to six weeks). Guan et al. (*20*) fed Angus steers monensin at 33 mg kg^{-1} of dry matter (DM) (approximately 250 mg $steer^{-1}$ day^{-1}) either a high concentrate (67% barley grain) or high forage (75% corn silage) diet and found short-term decreases (first four weeks) but not long-term decreases (subsequent eight weeks) in CH_4. Odongo et al. (*21*) fed lactating dairy cows a 60% forage diet (33% corn silage, 22% haylage, 5% alfalfa hay) with monensin content varying from 307.3 to 708.1 mg cow^{-1} day^{-1} and found a 7% reduction in grams of CH_4 cow^{-1} day^{-1} that was sustained over six months.

Hamilton et al. (*22*) fed lactating dairy cows a diet containing alfalfa hay as the primary forage (36% of DM) with 600 mg cow^{-1} day^{-1} of monensin and found no difference in CH_4 vs. controls after 14 or 60 days of continuous feeding. The variability of CH_4 emissions across these studies could be due in part to the different diet compositions, as well as the different concentrations of monensin included in the respective diets. More research is needed to conclusively determine the factors behind the variable results that have been observed.

Lipids

Feeding lipids, and more specifically, unsaturated fats, has been investigated in recent years as a rumen CH_4 mitigation method. The proposed effects of lipids in the rumen is two-fold: first, it is thought that lipids can be toxic to protozoa and methanogens in the rumen, and second, the process of rumen biohydrogenation (a process during which rumen microbes saturate the bonds of unsaturated fatty acids) can act as a H_2 sink that pulls H_2 out of the rumen pool and away from methanogens.

Much of the work with lipids has yielded conflicting results, akin to ionophores. Possible reasons for the inconsistencies are the type of lipids used (e.g., saturated, monounsaturated, and polyunsaturated fats), the dose level of the lipid, and possible adaptation by the rumen microbial ecosystem to the lipids (*23–25*). An important consideration is that there is a maximum percentage (approximately 6%) that lipids can be included in the diets of cattle after which the diet declines in palatability and negative effects on rumen microbes hinder the overall efficiency and performance of both beef and dairy cattle (*26*).

Condensed Tannins, Essential Oils, and Saponins

Recently, there has been an interest in using naturally occurring plant compounds as alternatives to antimicrobial CH_4-mitigating products such as monensin. Condensed tannins, saponins, and essential oils are three classes of such plant compounds that have been the focus of recent research, though much of this research has been done *in vitro*.

Condensed tannins are secondary plant compounds that are present in many forage species commonly consumed by beef and dairy cattle, such as the legume birdsfoot-trefoil. Condensed tannins have beneficial effects to ruminants when included in the diet at concentration less than 5% of dry matter (*27*). These effects include improved feed efficiency and reduced enteric CH_4 production. Condensed tannins are thought to affect rumen methane production by forming complexes with digestive enzymes and directly acting on rumen microorganisms, which inhibits fiber degradation, acetate production, and ultimately the amount of H_2 available to methanogens (*28–31*).

Saponins are another diverse group of plant extracts that have an anti-microbial effect in the rumen by destroying protozoa cell membranes, which leads to the subsequent death of those cells (*32*). The reduction of ruminal CH_4

appears to occur only from the reduction in protozoa and not direct effects on the methanogens (*26*, *32*). Holtshausen et al. (*33*) conducted both *in vitro* and *in vivo* studies examining the effects of saponin-containing *Yucca schidigera* and *Quillaja saponaria* on CH_4 production in dairy cattle. The researchers found that *in vitro* CH_4 production was reduced, which was attributed to decreased fermentation; however, no reduction of CH_4 was found *in vivo* (*33*). This study highlights the difficulty of translating *in vitro* results to live animal studies, with the long-term adaptation of the rumen microbes and the effects of saliva as two of the possible reasons for the inconsistent results.

Essential oils do not refer to a class of oils that must be provided in the diet of animals, as in essential amino acids, but rather refers to the essence or aromas that emanate from these dietary components. Examples of essential oils include garlic oil, capsaicin, anise oil, cinnamaldehyde, and eugenol (*34*). Some of the *in vivo* work with essential oils that found significant reductions in CH_4 has used sheep (*35*, *36*); nevertheless, more work needs to be done using beef and dairy cattle to determine ideal doses and if there are any adverse side effects (e.g., decreased milk quality).

To conclude, work conducted *in vivo* with cattle for all three of these classes of plant extracts is lacking, which makes estimations of their effectiveness in beef and dairy cattle difficult. Practically, the economic cost of these compounds' wide-scale use will need to be considered if and when it is found that the compounds are effective in reducing enteric CH_4 emissions.

Alternative Hydrogen Sinks

As previously mentioned, methanogenic archaea are some of the most competitive users of H_2; however, other H_2 sinks exist that can reduce the H_2 available to methanogens, thereby reducing the total amount of CH_4 produced in the rumen. In addition to the H_2 sink of unsaturated fatty acids, sulfur reducing and nitrate reducing bacteria can compete with the methanogens for H_2, though often the diet is low in the substrates required by these bacteria; therefore, the amount of H_2 used by these bacteria is usually minor. Keeping sulfate and NO_3^- concentrations low in the diets of beef and dairy cattle is critical because over a certain threshold the products of these reduction processes can build up in the rumen and are toxic to cattle (*11*, *37*). For example, the first step of NO_3^- reduction to ammonia, NO_3^- to nitrite (NO_2^-), is the fastest of all of the steps in the process, and if the diet contains too much NO_3^-, NO_2^- levels will increase (*38*). This increase in NO_2^- is undesirable because NO_2^- can be absorbed and convert hemoglobin to methemoglobin, thereby preventing oxygen from being transported to tissues throughout the body. Despite this risk, recent work has been conducted on gradually introducing nitrates into the diets of ruminants in an effort to gradually adapt the rumen microbial environment to the higher level of nitrates. Some of this work has shown promising reductions in CH_4 emissions (*37*); however, the practicality and cost of this mitigation measure must be considered.

Reductive acetogenesis (conversion of CO_2 to acetate) is another alternative hydrogen sink and one of the most desirable because acetate can be used as an energy source by the animal. Unfortunately, acetogens have a much lower affinity for H_2 than methanogens, which makes establishing populations of acetogens in the rumen difficult at best (*11*, *38*).

Precision Feeding

Precision feeding refers to a management scheme by dairy and beef operation owners where the animals are fed to precisely meet their specific nutrient requirements (e.g., early lactation dairy cow vs. late lactation dairy cow) and minimize excretion of nutrients and feed waste in the form of refusals (the feed offered to, but not consumed by the cattle). This type of management system requires beef and dairy producers utilizing confinement systems to carefully monitor the nutrient composition of individual feedstuffs and the ration that is delivered to the cattle. Over the past few decades, advances in technology have made this type of intensive management system more practical and economical for producers.

Precision feeding management can help reduce the GHG emissions that result from cattle waste, and, in particular, nitrogenous emissions. Ruminants are inefficient users of dietary protein when compared to non-ruminants due to the hydrolysis and deamination of proteins in the foregut by microbes that occurs before the digesta reaches the primary site of amino acid absorption (the small intestine). Reductions in N_2O emissions from cropland applied with manure and long-term manure storage systems can be achieved in part by reducing the total amount of N excreted by the animal. Precision feeding can help minimize the amount of N excreted to the environment, and consequently the N_2O emissions that would result from the land application of manure from cattle on a precision feeding regime.

Mitigation of Enteric Emissions through Production Efficiency

Production efficiency in beef and dairy production means improving the conversion of inputs (e.g., feed, water, etc.) into productive outputs (e.g., meat, milk), while limiting undesirable outputs (e.g., GHG). Many of the dietary strategies that have been outlined above improve the efficiency of beef and dairy production by reducing the amount of feed required to produce a unit of body gain or unit of milk. However, there are many other biological and management related mitigation measures that are often left out of the discussion of reducing GHG emissions from U.S. beef and dairy production systems.

The genetics of beef and dairy cattle are not often considered in studies concerning GHG emissions from animals; therefore, a more concerted effort is needed to examine the hereditability of traits associated with reduced environmental impact (e.g., residual feed intake). Undoubtedly, the improvement in performance of both beef and dairy cattle due to genetic progress has already lead to a reduction in the respective carbon footprints of their products (*39*), and further research into reducing the environmental impact of cattle-derived products through genetic selection holds great promise.

Biotechnologies, such as recombinant bovine somatotropin (rbST), anabolic implants, and beta-agonists, can improve the efficiency of milk and beef production and lower GHG emissions per unit of production. Using rbST can increase a single cow's milk production and decrease the amount of feed required to produce each kg of milk. Capper et al. (*9*) compared the environmental impact of milk production from a cow treated with or without rbST and found that using rbST reduced CH_4 emissions by 7.3% per unit of milk. Both anabolic implants and beta-agonists are in widespread use by the U.S. beef industry as growth promoters. Similar to rbST, these technologies can increase the amount of beef produced per unit of feed consumed; however, comprehensive analyzes of the environmental impact of these technologies have yet to be published.

In addition to genetic progress and biotechnologies, general management on dairies (e.g., reproductive programs, calf care, transition cow management, heat stress abatement, etc.) can have a significant impact on the efficiency of milk production on a dairy, and, consequently, the GHG produced per kg of milk (*40*). The beef industry has similar opportunities for reducing the carbon footprint of a kg of beef by improving management throughout the production chain. Two such examples are the reproductive efficiency of beef cows in the cow-calf sector and heat stress abatement in feedlots during the finishing phase.

The goal of most U.S. cow-calf producers is to have each cow calve every year and preferably within a narrow window of time (a season) to improve the consistency of the calves produced. Unfortunately, often times these producers do not check their cows for pregnancy at the end of the breeding season. According to USDA producer survey data, only 18% of cow-operations use rectal palpation to check for pregnancy (*41*). As a result, some non-pregnant cows continue to graze and produce CH_4 emissions over several months before the next calving season, at which time they will likely be removed from the herd. If these cows could be removed from the herd sooner and the overall reproductive management on U.S. cow-calf operations improved, there is a potential to reduce enteric GHG emissions by reducing the total U.S. beef cow herd.

Feedlot cattle are often exposed to extreme heat during the summer months. Heat stress in feedlot cattle has been shown to compromise the animals' health, welfare, and performance (*42*, *43*). Research examining heat stress mitigation measures has found that providing shade to feedlot cattle reduces the physiological signs of heat stress, and improves feed efficiency and carcass quality (*44*–*46*). Currently, shade structures are not used by all U.S. feedlots, as the most recent USDA survey found approximately 65% of feedlots provided no shade (*47*). A wider implementation of the use of shade in hot climate areas and other heat stress abatement measures in feedlots could reduce the overall carbon footprint of the beef industry by improving the efficiency of high quality beef production. Reproductive efficiency and heat stress are just two of the many examples of how management can affect the GHG produced per kg of beef; however, little research has been conducted using sophisticated modeling techniques to actually quantify the GHG savings of such management changes in either the beef or the dairy industries.

Mitigation of Manure-Derived Emissions

Manure storage and land applied manure are the other two major sources of GHG from the beef and dairy industries. The 2010 U.S. Environmental Protection Agency (EPA) inventory (*48*) for GHG emissions lists “manure management” as contributing 45 and 17.1 Tg CO_2 eq. of CH_4 and N_2O emissions respectively. Combined they equate to approximately 0.9% of total U.S. GHG emissions compared to just over 2% contributed by enteric CH_4 emissions (*48*). This manure management emission total includes the swine and poultry industries in addition to the beef and dairy industries. Despite the relatively small contribution to the U.S. GHG total, mitigating GHG emissions from animal manure is an area of active research.

Mitigation in Extensive Systems

In extensive systems, GHG emissions arise from the fecal and urine patches generated by the cattle grazing on pastures and rangeland. The CH_4 emissions arising from cattle waste under these conditions are negligible, because, as previously discussed, anaerobic conditions are needed to support the methanogenic archaea responsible for CH_4 emissions. However, N_2O emissions can occur from manure in extensive systems.

The total amount of N_2O produced will depend on the amount of N excreted by the cattle, the temperature, and soil conditions (e.g., pH, water content, etc.). Of the N that is excreted by grazing cattle, the fraction that is deposited in the soil as ammonium (NH_4^+) has the greatest potential to lead to N_2O emissions. This NH_4^+ is transformed first through the aerobic process of nitrification to NO_3^- and then through the anaerobic process of denitrification to N_2, with N_2O produced as one of the intermediates. Intervening in these microbial processes with nitrification inhibitors has shown promise in recent research. Urine patches treated with a nitrification inhibitor were found to have a 70% reduction in N_2O emissions (*49–51*), which is significant as urine patches can produce six times more N_2O than fecal patches (*52*).

Grazing cattle are often consuming an energy-limited diet, which leads to relatively higher N emissions compared to animals fed protein- and energy-balanced diets; therefore, providing energy supplements to grazing cattle may lead to a reduction in N_2O emissions (*53*, *54*). Wetter soils provide more ideal conditions for denitrifying bacteria, consequently, implementing drainage systems in pastures where possible, is a potential N_2O mitigation technique (*55*). Soil compaction by the hooves of cattle can lead to more anaerobic conditions that promote N_2O emissions; therefore, properly managing the stocking density and grazing frequency to limit soil compaction has the potential to reduce GHG emissions (*56*, *57*).

Mitigation in Intensive Systems

In intensive cattle systems, that include most dairy cattle and feedlot beef cattle, manure is often stored or treated before application to cropland. Manure storage includes both lagoons and manure piles. Dairies tend to use lagoons, due to the more liquid nature of dairy cattle manure compared to beef cattle and the use of water-utilizing flush systems to remove manure from barns. Some U.S. dairies (typically those with herd sizes under 200 cows) do not have long-term manure storage and rely instead on daily spreading of manure on cropland, a practice that results in insignificant GHG emissions (*58*). The design and storage capacity of manure lagoons on dairies varies considerably across U.S. dairies. In feedlot systems, most cattle are housed in earthen-floored pens and manure is allowed to accumulate in the animals' living area until it is scraped into piles and removed, usually every four to six months. In the beef system, N_2O contributes more than CH_4 to the GHG total from manure, while the reverse is true for the dairy industry (*58*). This is due to in part to the wider use of anaerobic manure lagoons in the dairy industry that promote CH_4 production. As previously discussed, using precision feeding schemes that reduce the N excreted by the animal is an important N_2O mitigation technique.

Mitigation of GHG from cattle manure in intensive systems can be achieved through anaerobic digestion, which is an attractive waste treatment practice because both pollution control and energy recovery can be achieved (*59*). Cattle manure, high in biodegradable material, is an ideal substrate for anaerobic digestion. Anaerobic digestion normally occurs within sealed vessels that promote the development of anaerobic microbes, which convert organic matter carbon into CH_4, CO_2, and other trace gases (*60*). This mixture of gases is referred to as biogas and can be combusted for electricity generation or further refined to produce a high quality natural gas that can be used in on-road vehicles. Due to the degradation of organic matter during anaerobic digestion, the potential of CH_4 emissions from the land application of the treated manure is reduced (*61*). In addition to the CH_4 reduction potential, Clemens and Huschka (*62*) found that anaerobically digested wastes may emit less N_2O than undigested waste because the easily degradable organic carbon used by the denitrifying bacteria is reduced. While U.S. cattle producers have already installed many anaerobic digesters, building these systems can be capital intensive and combusting biogas can lead to air quality issues, which has limited their wide scale construction.

Conclusion

Many GHG mitigation strategies exist for the U.S. cattle industries, some of which have the ancillary benefits of improved animal welfare and renewable energy generation. Ultimately, the GHG mitigation strategies discussed in this chapter should be evaluated and implemented in concert with other environmental (water, soil quality), animal welfare, and economic strategies. Consumer acceptance of new biotechnologies that could reduce emissions is yet another important consideration. This more holistic approach will require cooperation between researchers and industry, and a sophisticated understanding from regulators that these strategies will not take the form of a one-size-fits-all solution, but rather vary from farm-to-farm depending on climate, soils, animal-type, business model, etc.

References

1. Pitesky, M. E.; Stackhouse, K. R.; Mitloehner, F. M. *Adv. Agron.* **2009**, *103*, 1–40.
2. IPCC; *Climate change 2007: The physical life science basis. Group I contribution to the fourth assessment report of the IPCC*; Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press: New York, NY, 2007; pp 1−996.
3. De Boer, I. J. M. *Livest. Prod. Sci.* **2003**, *80*, 69–77.
4. Velthof, G. L.; van Beusichem, M. L.; Oenema, O. *Environ. Pollut.* **1998**, *102*, 173–178.
5. Kaspar, H. F; Tiedje, J. M. *Appl. Environ. Microbiol.* **1981**, *41*, 705–709.
6. Casey, J. W.; Holden, N. M. *Agr. Syst.* **2005**, *86*, 97–114.
7. NASS. Cattle. http://usda.mannlib.cornell.edu/usda/current/Catt/Catt-07-23-2010.pdf (accessed Dec. 6, 2010).
8. NASS. Milk Production. http://usda.mannlib.cornell.edu/MannUsda/viewDocumentInfo.do?documentID=1103 (accessed Dec. 6, 2010).
9. Capper, J. L.; Cady, R. A.; Bauman, D. E. *J. Anim. Sci.* **2009**, *87*, 2160–2167.
10. Janssen, P. H. *Anim. Feed Sci. Tech.* **2010**, *160*, 1–22.
11. Ellis, J. L.; Dijkstra, J.; Kebreab, E.; Bannink, A.; Odongo, N. E.; McBride, B. W.; France, J. *J. Agr. Sci.* **2008**, *146*, 213–233.
12. Janssen, P. H.; Kirs, M. *Appl. Environ. Microbiol.* **2008**, *74*, 3619–3625.
13. Johnson, K. A.; Johnson, D. E. *J. Anim. Sci.* **1995**, *73*, 2483–2492.
14. Owens, F. N.; Secrist, D. S.; Hill, W. J.; Gill, D. R. *J. Anim. Sci.* **1998**, *76*, 275–286.
15. Bauman, D. E.; Griinari, J. M. *Annu. Rev. Nutr.* **2003**, *23*, 203–227.
16. Russell, J.; Houlihan, A. *FEMS Microbiol. Rev.* **2003**, *27*, 65–74.
17. Chapman, H. D.; Jeffers, T. K.; Williams, R. B. *Poultry Sci.* **2010**, *89*, 1788–1801.
18. Tedeschi, L. O.; Fox, D. G.; Tylutki, T. T. *J. Environ. Qual.* **2003**, *32*, 1591−1602.
19. Ipharraguerre, I. R.; Clark, J. H. *Anim. Feed Sci. Tech.* **2003**, *106*, 39–57.
20. Guan, H.; Wittenberg, K. M.; Ominski, K. H.; Krause, D. O. *J. Anim. Sci.* **2006**, *84*, 1896–1906.
21. Odongo, N. E.; Bagg, R.; Vessie, G.; Dick, P.; Or-Rashid, M. M.; Hook, S. E.; Gray, J. T.; Kebreab, E.; France, J.; McBride, B. W. *J. Dairy Sci.* **2007**, *90*, 1781–1788.
22. Hamilton, S. W.; DePeters, E. J.; McGarvey, J. A.; Lathrop, J.; Mitloehner, F. M. *J. Environ. Qual.* **2009**, *39*, 106–114.
23. Beauchemin, K. A.; McGinn, S. M.; Benchaar, C.; Holtshausen, L. *J. Dairy Sci.* **2009**, *92*, 2118–2127.

24. Hristov, A. N.; Vander Pol, M.; Agle, M.; Zaman, S.; Schneider, C.; Ndegwa, P.; Vaddella, V. K.; Johnson, K.; Shingfield, K. J.; Karnati, S. K. R. *J. Dairy Sci.* **2009**, *92*, 5561–5582.
25. Johnson, K. A.; Kincaid, R. L.; Westberg, H. H.; Gaskins, C. T.; Lamb, B. K.; Cronrath, J. D. *J. Dairy Sci.* **2002**, *85*, 1509–1515.
26. Beauchemin, K. A.; McAllister, T. A.; McGinn, S. M. *CAB Rev.* **2009**, *35*, 1–18.
27. Min, B. R.; Barry, T. N.; Attwood, G. T.; McNabb, W. C. *Anim. Feed Sci. Tech.* **2003**, *106*, 3–19.
28. Barry, T. N.; Manley, T. R. *Brit. J. Nutr.* **1984**, *51*, 493–504.
29. Jones, G. A.; McAllister, T. A.; Muir, A. D.; Cheng, K. J. *Appl. Environ. Microbiol.* **1994**, *60*, 1374–1378.
30. McMahon, L. R.; McAllister, T. A.; Berg, B. P.; Majak, W.; Acharya, S. N.; Popp, J. D.; Coulman, B. E.; Wang, Y.; Cheng, K. J. *Can. J. Plant Sci.* **2000**, *80*, 469–485.
31. Scalbert, A. *Phytochemistry* **1991**, *30*, 3875–3883.
32. Patra, A. K.; Saxena, J. *Nutr. Res. Rev.* **2009**, *22*, 204–219.
33. Holtshausen, L.; Chaves, A. V.; Beauchemin, K. A.; McGinn, S. M.; McAllister, T. A.; Odongo, N. E.; Cheeke, P. R.; Bencharr, C. *J. Dairy Sci.* **2009**, *92*, 2809–2821.
34. Calsamiglia, S.; Busquet, M.; Cardozo, P. W.; Castillejos, L.; Ferret, A. *J. Dairy Sci.* **2007**, *90*, 2580–2595.
35. Hess, H. D.; Beuret, R. A.; Lotscher, M.; Hindrichsen, I. K.; Machmuller, A.; Carulla, J. E.; Lascano, C. E.; Kreuzer, M. *Anim. Sci.* **2004**, *79*, 177–189.
36. Mao, H.; Wang, J.; Zhou, Y.; Liu, J. *Livest. Sci.* **2010**, *129*, 56–62.
37. van Zijderveld, S. M.; Gerrits, W. J. J.; Apajalhti, J. A.; Newbold, J. R.; Dijkstra, J.; Leng, R. A.; Perdok, H. B. *J. Dairy Sci.* **2010**, *93*, 5856–5866.
38. Weimer, P. J. *J. Anim. Sci.* **1998**, *76*, 3114–3122.
39. Capper, J. L.; Castaneda-Gutierrez, E.; Cady, R. A.; Bauman, D. E. *Proc. Natl. Acad. Sci., U.S.A.* **2008**, *105*, 9668–9673.
40. Place, S. E.; Mitloehner, F. M. *J. Dairy Sci.* **2010**, *93*, 3407–3416.
41. USDA. *Beef 2007-08, Part II: Reference of Beef Cow-calf Management Practices in the United States, 2007-08*; USDA:APHIS:VS, CEAH: Fort Collins, CO, 2009.
42. Armstrong, D. V. *J. Dairy Sci.* **1994**, *77*, 2044–2050.
43. Hahn, G. L. *J. Anim. Sci.* **1999**, *77*, 10–20.
44. Gaughan, J. B.; Bonner, S.; Loxton, I.; Mader, T. L.; Lisle, A.; Lawrence, R. *J. Anim. Sci.* **2010**, *88*, 4056–4067.
45. Mitlöhner, F. M.; Galyean, M. L.; McGlone, J. J. *J. Anim. Sci.* **2002**, *80*, 2043–2050.
46. Mitlöhner, F. M.; Morrow-Tesch, J. L.; Wilson, S. C.; Dailey, J. W.; McGlone, J. J. *J. Anim. Sci.* **2001**, *79*, 1189–1193.
47. USDA. *Part III: Health Management and Biosecurity in U.S. Feedlots, 1999*; USDA:APHIS:VS, CEAH, National Animal Health Monitoring System: Fort Collins, CO. 2000.

48. US EPA. Inventory of U.S. greenhouse gas emissions and sinks: 1990-2008. U.S. Environ. Protection Agency, Washington, D.C. http://www.epa.gov/climatechange/emissions/usinventoryreport.html (accessed Dec. 13, 2010).
49. Di, H. J.; Cameron, K. C. *Soil Use Manage.* **2003**, *19*, 284–290.
50. Di, H. J.; Cameron, K. C. *Agr. Ecosys. Environ.* **2005**, *109*, 202–212.
51. Di, H. J.; Cameron, K. C. *Biol. Fert. Soils* **2006**, *42*, 472–480.
52. Oenema, O.; Velthof, G. L.; Yamulki, S.; Jarvis, S. C. *Soil Use Manage.* **1997**, *13*, 288–295.
53. Kebreab, E.; France, J.; Beever, D. E.; Castillo, A. R. *Nutr. Cycl. Agroecosys.* **2001**, *60*, 275–285.
54. Nielsen, N. M.; Kristensen, T.; Nørgaard, P.; Hansen, H. *Livest. Prod. Sci.* **2003**, *81*, 293–306.
55. de Klein, C. A. M.; Barton, L.; Sherlock, R. R.; Li, Z.; Littlejohn, R. P. *Aust. J. Soil. Res.* **2003**, *41*, 381–399.
56. de Klein, C. A. M.; Smith, L. C.; Monaghan, R. M. *Agr. Ecosys. Environ.* **2006**, *112*, 192–199.
57. Luo, J.; Tillman, R. W.; Ball, P. R. *Soil Biol. Biochem.* **2000**, *32*, 497–509.
58. USDA. *U.S. Agriculture and Forestry Greenhouse Gas Inventory: 1990-2001.* Global Change Program Office, Office of the Chief Economist, U.S. Department of Agriculture. Technical Bulletin No. 1907. 2004. 164 pp.
59. Amon, B.; Amon, T.; Boxberger, J.; Alt, C. *Nutr. Cycl. Agroecosys.* **2001**, *60*, 103–113.
60. Clemens, J.; Trimborn, M.; Weiland, P.; Amon, B. *Agr. Ecosys. Environ.* **2006**, *112*, 171–177.
61. Amon, B.; Kryvoruchko, V.; Amon, T.; Zechmeister-Boltenstern, S. *Agr. Ecosys. Environ.* **2006**, *112*, 153–162.
62. Clemens, J.; Huschka, A. *Nutr. Cycl. Agroecosys.* **2001**, *59*, 193–198.

Chapter 24

Improved Productivity Reduces Greenhouse Gas Emissions from Animal Agriculture

Judith L. Capper[*]

**Department of Animal Sciences, Washington State University,
Pullman, WA, U.S.A.
[*]E-mail: capper@wsu.edu**

As the global population increases, more milk, meat and eggs need to be produced using fewer resources and with a lower environmental impact. Over the past century, improving productivity has considerably reduced the carbon footprint of dairy and beef production, yet consumers often perceive extensive, 'traditional' systems to have a low carbon footprint. Scientific analysis shows that intensive animal production systems have a lower carbon footprint than extensive systems - improved education of consumers, retailers and media is therefore required to overcome popular misconceptions relating to the carbon footprint of animal agriculture.

Introduction

In 1800, each U.S. farm could only produce enough food to feed one other family. In the wake of considerable improvements in productivity, each farmer currently produces enough food to feed an average of 125 other people. The global population is predicted to increase to approximately 9.5 billion people in the year 2050. This will increase total food requirements by 70% compared to the present day (*1*) as a function of population size and the augmented demand for milk and meat protein resulting from greater global affluence. Assuming the present competition for energy, land and water continues, resources available for agricultural production will decrease with increased population growth. The global livestock industries therefore face the challenge of producing sufficient animal-source foods to meet consumer demand, using a finite resource base.

The environmental impact of livestock farming is one of the most commonly discussed issues within food production. A lexicon of previously-unfamiliar terms including “carbon footprint”, “sustainability” and “local food” have entered everyday conversation via media articles, blog posts and restaurant menus. Bookstores, whose food sections were previously limited to publications on cooking and food preservation, now stock books that aim to inform the consumer as to the most environmentally-friendly and socially responsible mechanisms for buying and preparing food. The benefits of “knowing your farmer”, “buying local” and “meatless Monday” schemes are extolled by celebrities on television and in advertising campaigns. In a world where less than 2% of people are employed within agriculture, a growing interest in and awareness of where food comes from is laudable and could considerably improve the consumers' image of agriculture. This is exemplified by the rise of “ethical consumerism”, described by Singer and Mason (*2*) as an increasing interest in the way in which food is produced, the practices employed and a concern for low environmental impact, high animal welfare and optimal worker conditions. Nonetheless, popular perceptions of sustainable agriculture are often directed towards traditional systems, organic production or farms that supply only the local geographic area. Many consumers therefore consider conventional large-scale agriculture to exist in direct contrast to the sun-lit rustic image of traditional, low-input, extensive food production, a contrast which is further highlighted by niche marketing campaigns and information within popular movies such as “Food Inc”. Although it is widely understood that improving efficiency reduces expense, resources and waste, the consumer often appears to consider “efficiency” to have negative connotations when applied to food production. Animal proteins are generally considered as staple foods in U.S. diets, however, concern over the perceived environmental impact of conventional animal production may threaten social license to operate in future. This article will discuss the effects of advances in productivity and efficiency in the U.S. livestock industries upon the environmental impact and carbon footprint of modern food production.

The Link between Efficiency, Productivity, and the Carbon Footprint

Imagine an bakery that produces bread from Monday to Friday each week. Although the factory only produces bread for five days per week, fixed costs of $5,000 (rent, taxes, etc) are incurred each day, regardless of productivity. If the factory produces 100,000 loaves over this time period, the fixed costs can be divided by the total output [($5,000 x 7 days)/100,000 loaves = $0.35/loaf] and the bread priced accordingly. If the bakery improves productivity so that 200,000 loaves are manufactured in the same time period, efficiency improves and fixed costs are spread over greater output ($0.18/loaf). The same concept can be applied to livestock production and is known as the “dilution of maintenance” effect. All animals have a maintenance nutrient requirement that must be fulfilled each day to support vital functions and minimum activities – this may be considered as the “fixed cost” of livestock production. Improving productivity such that a greater amount of milk or meat is produced in a set period of time per unit of animal input thus reduces the total maintenance cost per unit of food produced. Maintenance nutrients may be considered a proxy for resource use (feed, land, water, fossil fuels) and waste output (manure, greenhouse gases (GHG)). Improving productivity therefore reduces resource use and waste output per unit of food. From an environmental standpoint, GHG (CH_4, N_2O and CO_2) and the carbon footprint (the sum of all GHG expressed as CO_2-equivalents) may be considered one of the most important waste outputs.

Improved Dairy Productivity Reduces the Carbon Footprint

The phrase "dairy farming in the 1940's" conjures bucolic images of a family farm with a red barn, green pastures and a small herd in which cows were named Bessie, Marigold and Buttercup. The farm children did chores each day, and the farmer milked cows by hand while seated on a three-legged stool. This rural utopia appeared to be an untroubled life where milk could be drunk straight from the cow, neither cows nor manure produced GHG and the small tractor used to plow the fields used small quantities of fuel from an infinite supply. By contrast, the modern dairy farm with streamlined milking equipment, pasteurization processes, anaerobic digesters and specialized labor appears to some as a futuristic aberration. The fact that cows produce CH_4 through enteric fermentation has been known for many years, yet the link between climate change and livestock production is a relatively recent notion. The perception therefore exists that modern livestock production causes climate change, whereas extensive systems akin to historical management are far more environmentally-friendly. It is interesting to note that the CH_4 and N_2O emissions from enteric fermentation and manure produced by the 60 million buffalo that roamed the U.S. plains until mass extinction in 1880 (*3*) are equal to double the carbon footprint produced by the U.S. dairy industry in 2007 (Figure 1).

In 1944, the U.S. dairy population peaked at 25.6 million dairy cattle, producing 53.0 billion kg of milk (*4*). The average herd contained six cows that were fed a pasture-based diet with occasional supplemental corn or soy (*5*). Artificial insemination was in its infancy and neither antibiotics nor supplemental hormones were available for animal use. By contrast, the 2007 U.S. dairy herd contained 9.2 million cows producing 84.2 billion kg milk, the gains in productivity and efficiency facilitated by improvements in management, nutrition, genetics and the application of new technologies that led to a four-fold increase in milk yield per cow between 1944 and 2007 (*5*). This can be considered a proof of concept for the dilution of maintenance effect – increased milk production per cow means that fewer lactating animals are required to produce the same quantity of milk and the size of the supporting herd (dry cows, bulls, heifer and bull replacements) is also reduced. Indeed, compared to 1944, the 2007 U.S. dairy industry required only 21% of the dairy population and therefore 23% of the feedstuffs, 10% of the land and 35% of the water to produce a set quantity of milk. Manure output per unit of milk produced in 2007 was 24% of that in 1944 and the total carbon footprint per unit of milk was reduced by 63%. Despite the increase in total milk production between 1944 and 2007, the total carbon footprint for the entire dairy industry was reduced by 41%.

Regional Variation in Dairy Production's Carbon Footprint

The improvement in efficiency is not confined to the U.S.: Cederburg et al. (*6*) describe a 20% reduction in carbon footprint per kg of milk produced in Sweden between 1990 and 2005 and attribute this to improved productivity. If we examine international trends, major milk-producing regions (U.S, Canada, New Zealand, Europe) have all improved milk yield per cow since the 1960's, the rate of improvement varying from 129 kg/y and 117 kg/y for the U.S. and Canada to 77 kg/y and 24 kg/y for Europe and New Zealand (*7*). The environmental effects of regional variations in productivity are exemplified by the results of a recent FAO (*8*) report that modeled GHG emissions from dairy production using life cycle analysis (LCA). As intensity of production declines and the average milk yield shifts from approximately 9,000 kg/cow for North America to ~250 kg/cow for Sub-Saharan Africa, the carbon footprint increases from 1.3 kg CO_2-eq/kg milk to 7.6 kg CO_2-eq/kg milk (Figure 2). Sustainability is often defined as having three inter-related components: environment, economic and social, with sustainability occurring through a balance of these factors. When assessing the sustainability of dairy systems the question should not therefore be limited to the environmental impact of the dairying within a specific region, but must also consider the economic and social implications. While the FAO data could provoke the conclusion that all regions should adopt North American and Western European-style production systems, or that dairying should be focused in these areas and be discouraged in less productive regions such as Sub-Saharan Africa and South Asia, the significant social (both status and nutritional) and economic value of dairying in less-developed regions must not be underestimated. The challenge for global dairy production is therefore to optimize sustainability within each region rather than prescribing the best "one-size-fits-all" global system. Nonetheless, improving productive efficiency would be predicted to reduce the carbon footprint in all regions.

Improving Beef Productivity Reduces Carbon Footprint per Kilogram of Beef

Productivity has improved substantially in the U.S. beef industry, with average beef-carcass yield per animal increasing from 274 kg in 1977 to 351 kg in 2007 (*9*, *10*). Management advances including improved genetic selection, ration formulation and growth-enhancing technology use over this time period also conferred an increase in growth rate, reducing the total days from birth to slaughter from 609 days in 1977, to 485 days in 2007. In combination with increased beef yield per animal reducing the size of the supporting population, producing a set quantity of beef in 2007 required 70% of the animals, 81% of the feed, 88% of the water and 67% of the land needed by the 1977 system. Along with the changes in resource use, improved productivity meant that manure and

GHG emissions were considerably reduced, with a 16% decrease in the carbon footprint per unit of beef (*11*).

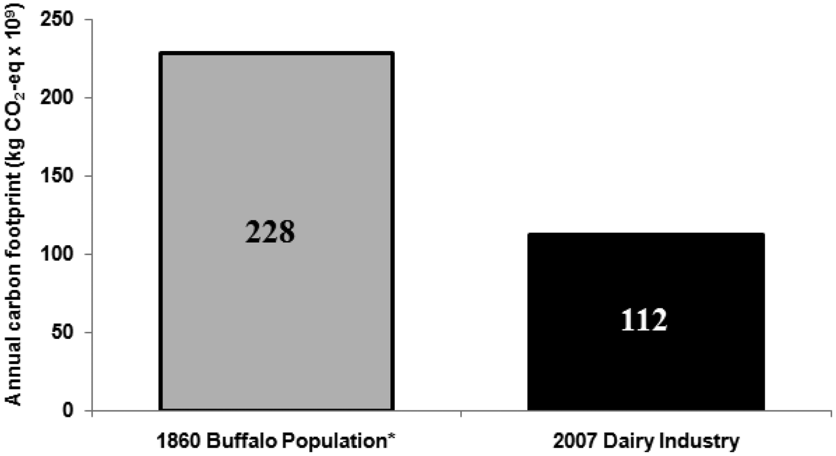


*Figure 1. Comparative annual carbon footprints of the U.S. 1860 buffalo population and 2007 dairy industry (5). *CH_4 and N_2O emissions are based on forage dry matter intakes for age-appropriate liveweights and population dynamics, emission factors from U.S. EPA (39).*

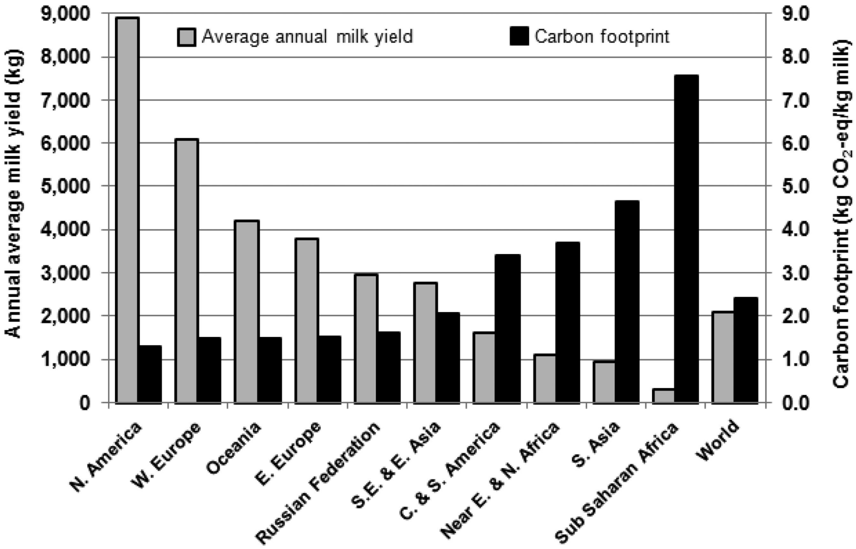


Figure 2. Average annual milk yield and carbon footprint per kg of milk for selected global regions (8).

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

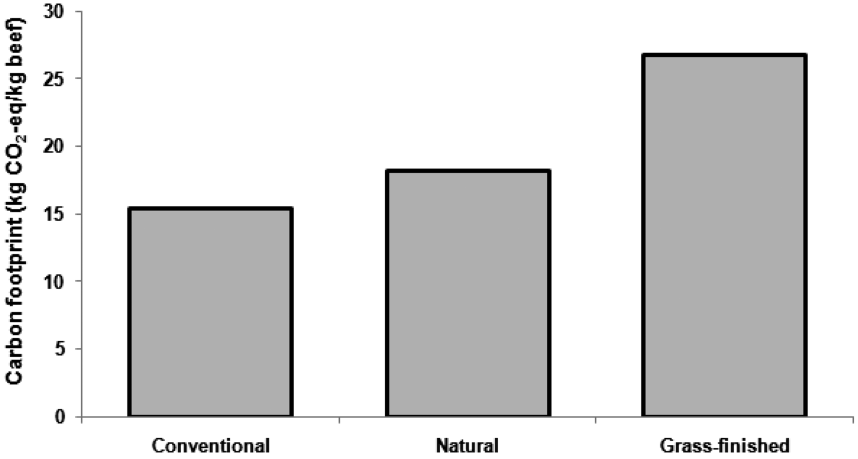


Figure 3. Carbon footprint per kg of beef produced in three different systems. Carbon footprints based on full-system analyses with full productivity-enhancing technology use (conventional) and feedlot finishing; no productivity-enhancing technology use plus feedlot finishing (natural) or no productivity-enhancing technology use plus grass finishing (grass-finished; (17)).

A positive relationship exists between environmental and economic impact. Survey data indicates that consumers desire food products that are affordable, animal welfare-friendly and have a low environmental impact (*12*). Nonetheless, the popular view is that affordability is mutually incompatible with either of the latter factors. This view is fostered by media coverage relating to "cheap" food, suggesting that grass-finished systems are superior to conventional feedlot beef production in terms of nutritional quality, GHG emissions and animal welfare (*13*). The increased economic cost of products labeled "organic", "natural" or "hormone-free" (*14*) further supports the subliminal impression that conventional production must occur at the expense of environmental, animal or human health. The FAO (*15*) concludes that it is essential to continue to intensify livestock production in order to maintain the efficiency gains that improve environmental and economic sustainability. By contrast, consumers often assume that extensive, pasture-based beef systems where cattle are finished on grass have a lower carbon footprint than conventional feedlot systems.

Pelletier et al. (*16*) reported that GHG emissions per kg of beef were highest in pasture-finished systems compared to feedlots. This result seems intuitively incorrect – a conventional system that finishes animals on corn-based diets grown with significant fertilizer inputs, transports both feed and animals across the U.S.A. and houses animals in confinement would seem to have an intrinsically higher environmental impact that a grass-finishing system. Nonetheless, from a biological viewpoint, the results are easy to explain. Growth rates are considerably lower in animals finished on grass and it is difficult to achieve high slaughter weights, therefore grass-finished cattle are usually slaughtered at around 486 kg at 679 days of age, compared to 569 kg at 453 days of age in a conventional system. Capper (*17*) demonstrated that as a consequence of the reduced slaughter weight, 4.5 total animals (slaughtered animals plus the supporting population required to produce calves for rearing) are required to produce 363 kg of hot-carcass weight beef in a grass-finished system compared to 2.6 total animals in a conventional system. When combined with the increased time required to grow animals to slaughter weight, this increases the carbon footprint per kg of grass-finished beef by 74% (Figure 3). Moreover, the increased land required for grass-finished production renders whole-scale conversion of the U.S. beef production system to grass-finished production practically impossible. However, if we assume it would somehow be achievable and that beef production was maintained at 11.8 billion kg as seen in 2009 (*18*), this would require 64.6 million animals to be added to the national herd, with a 53.1 million ha increase in land use (75% of the area of Texas). Furthermore, the increase in carbon emissions would be equal to adding 26,465,074 cars to the road on an annual basis.

Proponents of pasture-finishing may counter-argue that although decreases in productivity increase GHG emissions from animal sources, the quantity of carbon sequestered by pasture-based systems compensates for reduced efficiencies (*19*). Sound data on carbon sequestration is notably lacking from environmental literature and this is one area where future research would pay dividends in terms of improving knowledge and understanding. It is important to note that between half and two-thirds of conventional growing beef animals' lives and the entirety of the supporting population's lives are based on forage and pasture. Differences attributed to carbon sequestration between systems could therefore only be attributed to the finishing period. Considerable carbon sequestration into pastureland would have to occur in order to outweigh the total GHG emissions resulting from the combination of a greater population size, extra days required to finish animals on pasture, and increased CH_4 emissions emitted from animals fed predominantly forage diets, particularly given that each kg of CH_4 or N_2O emitted has a global warming potential 25x or 298x respectively when compared to CO_2 indexed as 1 (*20*)

Advances in Monogastric Animal Productivity

Compared to ruminant production, swine and poultry industries are generally considered to be less environmentally-threatening with regards to climate change. Estimates of the carbon footprint of monogastric animal protein production range from 2.8 to 4.5 kg CO_2/kg pork (*21–23*) and 1.9 to 2.9 kg CO_2/kg chicken (*6*, *24*, *25*). Nonetheless, given the increase in poultry and swine consumption predicted to occur over the next 40 years (*26*), further efficiency improvements are necessary within these industries in order to reduce overall environmental impact over time. Vertical integration and consolidation within both industries considerably improved productivity over the past 50 years. According to historical USDA data, between 1963 and 2009, average U.S. dressed swine carcass weight increased by 27 kg, from 65 kg to 92 kg (*4*). This allowed total dressed weight (slaughtered animals x average dressed weight) to increase from 5.4 billion kg to 10.5 billion kg (a 92% increase) while slaughter numbers only increased by 44% (35 million animals). Despite the increase in slaughter numbers, the U.S. swine breeding population decreased from 9,117 thousand head to 5,850 thousand head, as a function of both increased litter size and a greater number of farrowings per year. As demonstrated by the historical beef comparison, the increase in average dressed carcass weight combined with the smaller supporting population would be expected to have a positive mitigation effect on carbon footprint per kg of pork.

Similarly, average chicken slaughter weight increased from 1.61 kg to 2.54 kg over the same time period (1963-2009), facilitating an 594% increase in chicken production (3.17 billion kg to 29.4 billion kg) with only a 341% increase in slaughter numbers (1.96 billion head to 8.66 billion head; USDA, 2009). Growth rates and feed efficiency also improved considerably over the past 60 years, reducing the time period from birth to slaughter from 90 days to less than 40 days (*27*). Evidence from feeding studies involving heritage-style breeds suggests that although nutrition and management have played a significant role, the majority of this improvement has occurred through genetic gain (*28*, *29*). The question as to how efficient livestock production can become is often posed. Given the already high feed efficiencies and growth rates seen in the pork and poultry industries, there may be less opportunity to improve these metrics than in the beef industry, yet the use of by-products from the human feed and fiber industries is relatively low in monogastric diets. The beef and dairy industries play an invaluable role in converting inedible forages and by-products from human food and fiber production into high-quality animal protein. As concern already exists as to the extent of human-edible food used for animal production (*30*), increased use of by-product feeds which by their nature have a considerably lower carbon footprint and effect upon human food stocks, may be a potential avenue to further mitigate carbon emissions from monogastric animals.

The Value of the "Exact" Number versus the Delta

An observant reader may note that the results discussed with reference to both historical vs. modern systems and conventional vs. grass-finished beef have been expressed as percentage changes rather than absolute numbers. The need to quantify the carbon footprint of animal production is generally recognized, however, it is this author's view that comparative studies which provide insight into the relative impact of systems or production practices and thus the possibilities to improve the delta, are more valuable. This is especially pertinent to carbon footprints quantified via LCA, which is specific to particular time-points and regions, and governed by system boundaries. The carbon footprint of beef production has been quantified using LCA in the U.S.A., Canada, Brazil, Sweden, Australia and Japan (Figure 4); and a global analysis is currently being undertaken by the FAO. However, variation in methodology, boundaries and time-points for each system render direct comparisons impossible. The need for a coordinated international methodology has been noted by many industry groups and non-governmental organizations, yet LCA and other methods are still in developmental infancy, with significant data gaps. The urgency of current consumer, retailer and policy-maker concerns relating to the carbon footprint of animal production, suggests that rather than waiting for the science to evolve further, systems and management practices that mitigate carbon emissions based on credible science and biology should be implemented immediately.

Food Transport – Mythical Unicorn of the Locovore Movement

The view that food should be produced locally often appears in tandem with the historical ideal of traditional farming. In bygone days, a significant amount of time was spent shopping for food at the butcher, baker, fishmonger and grocer within the local town. The same voices crying out against modern agriculture often lament the loss of this lifestyle and argue against large-scale grocery stores that carry food from national and international sources. There is no doubt that lifestyles have changed considerably in the past 60 years – the suggestion by Michael Pollan (*31*) that "To grow sufficient amounts of food using sunlight will require more people growing food - millions more" is entirely laudable if the current 9% of the U.S. population who are unemployed simply decided to work in agriculture. Realistically however, moving to an extensive "sun-food" system where fossil fuels are replaced by human labor negates the improvements in efficiency made over time and neglects to consider the energy inputs and carbon output associated with human labor, let alone the negative trade-offs occurring from shirts in labor patterns from, for example, healthcare, education or construction to agriculture. The perception that transport comprises a significant proportion of the total carbon footprint of animal products is simply untrue. Recent analyses demonstrate that 7.7% of the GHG emissions of a unit of milk (*32*) and 0.75% of a unit of beef (*11*) can be attributed to transport.

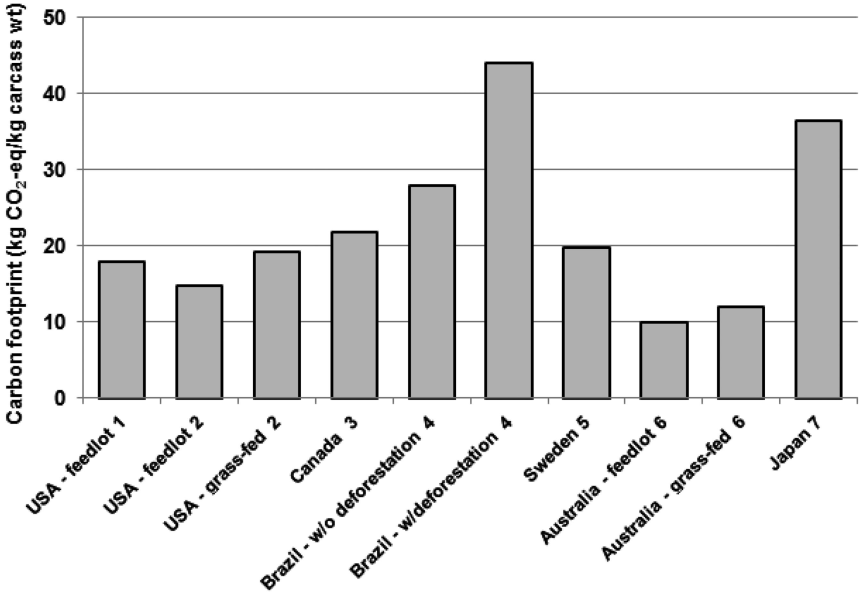


Figure 4. Variation in the carbon footprint per kg of beef according to region and system. (Sources: [1](11); [2](16); [3](35); [4](38); [5](6); [6](37); [7](36).)

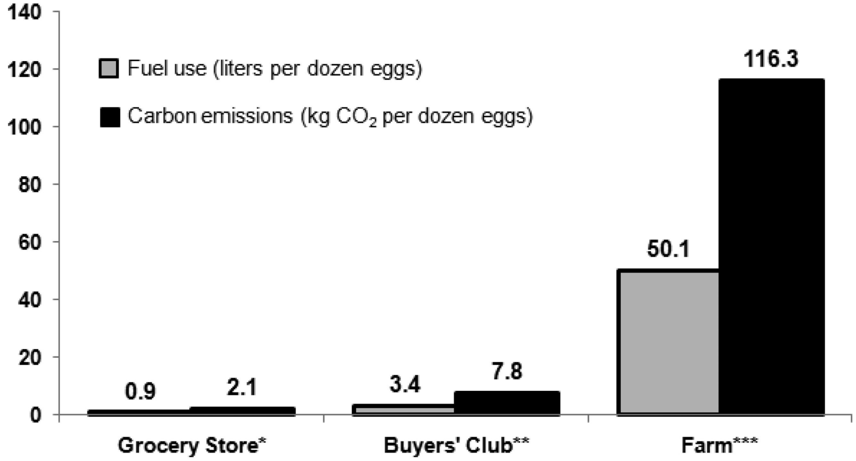


*Figure 5. Fuel use and carbon emissions associated with purchasing one dozen eggs from three different sources. * 3,862 km tractor-trailer round-trip (23,400 dozen egg capacity) plus 8 km consumer's car round-trip (1 dozen egg capacity); ** 477 km pick-up truck round-trip (1,740 dozen egg capacity) plus 16 km consumer's car round-trip (1 dozen egg capacity); *** 482 km consumer's car round-trip (1 dozen egg capacity); Methodology and all fuel efficiencies as described in Capper et al. (7).*

Niche extensive markets often seek to differentiate from conventional production on the basis of reduced fossil fuel use for transport and therefore implicit reductions in carbon emissions. For example, one farm website (*33*) proudly states that “We do not ship anything anywhere. We encourage folks to find their local producers and patronize them.” However, the same website describes a “Buyers' Club” where food is mass-transported to locations an average of 239 km from the farm for consumer to collect and also includes the following quote: “I drive to <<*Farm*>> 150 miles (241 km) one way in order to get clean meat for my family.” Using details of vehicle carrying capacity and fuel efficiency derived from Capper et al. (*7*), the fuel use and consequent carbon emissions associated with buying one dozen eggs were assessed using three points of purchase: the local grocery store, the buyers' club or the farm. Figure 5 shows that productivity is again the key factor – improved carrying capacity of the tractor-trailer outweighed both the low fuel efficiency and the distance that eggs were transported across the country to the grocery store, with 0.9 liters fuel used per dozen eggs. Intermediate productivity and carrying capacity in the buyers' club example increased fuel use to 3.4 liters per dozen eggs and the low productivity (one dozen eggs per car) involved with buying the eggs directly from the farm increased fuel use 56-fold (50.1 liters) compared to the grocery store example. When emissions from gasoline and diesel were considered (*34*), carbon emissions per dozen eggs were highest for the farm example (116.3 kg CO_2/dozen eggs), intermediate for the buyers' club and lowest in the grocery store example (2.1 kg CO_2/dozen eggs). The “feel-good” factor involved with traveling a round-trip of 482 km to purchase eggs from that are perceived to be of higher quality directly from a farm certainly contributes to the social sustainability of this choice. Nonetheless, the choice carries huge economic and environmental consequences. Consumer choice appears to be one of the paramount issues for retailers, marketers and policy-makers, nonetheless, the choice should be an educated one based on science and logic rather than philosophical assumptions.

Implications

It is clear that the livestock industry faces a challenge in producing sufficient animal-source foods to supply the needs of the growing global population, whilst reducing environmental impact. Possibly the most significant question relating to this issue, is how to overcome the popular perception of modern agriculture as being environmentally unfavorable. Science shows that advances in productivity garnered through improved management and technology use improve the carbon footprint per unit of food, yet consumers, retailers and mainstream media do not appear to have been convinced. Demonization of specific sectors (e.g. feedlot beef or eggs purchased from the grocery store) in favor of niche markets that intuitively seem to have a lower carbon footprint further propagate the idea that conventional production and mass food transport are undesirable. In a region where food is readily available and represents a relatively small proportion of disposable income, consumers are afforded the luxury of making choices according to production system or technology use, yet many developing regions exist where the simple need for food negates such concerns. It is hoped that improved education will shift consumer understanding away from perceptions and erroneous ideas provided by niche marketers or special interest groups towards choices that are made on the basis of sound science.

References

1. Food and Agriculture Organization of the United Nations. *How to Feed the World in 2050*; FAO: Rome, Italy, 2009.
2. Singer, P.; Mason, J. *The Way We Eat: Why Our Food Choices Matter*, 1st ed.; Rodale Books: Emmaus, PA, 2006.
3. Roe, F. G. *The North American Buffalo: A Critical Study of the Species in its Wild State*; University of Toronto Press: Toronto, Canada, 1951.
4. Data and Statistics. http://www.nass.usda.gov/Data_and_Statistics/Quick_Stats/index.asp.
5. Capper, J. L.; Cady, R. A.; Bauman, D. E. *J. Anim. Sci.* **2009**, *87*, 2160–2167.
6. Cederberg, C.; Sonesson, U.; Henriksson, M.; Sund, V.; Davis, J. *Greenhouse gas emissions from Swedish production of meat, milk and eggs: 1990 and 2005*; The Swedish Institute for Food and Biotechnology: Gothenburg, Sweden, 2009.
7. Capper, J. L.; Cady, R. A.; Bauman, D. E. In *Demystifying the environmental sustainability of food production*, Proceedings of the Cornell Nutrition

Conference, Syracuse, NY, October 20−22, 2009; Cornell University: Syracuse, NY, 2009.

8. Food and Agriculture Organization of the United Nations. *Greenhouse Gas Emissions from the Dairy Sector: A Life Cycle Assessment*; FAO: Rome, Italy, 2010.
9. USDA. *Livestock Slaughter Annual Summary 1977*; USDA: Washington, DC, 1978.
10. USDA/NASS. *Livestock Slaughter 2007 Summary*; USDA: Washington, DC, 2008.
11. Capper, J. L. *J. Anim. Sci.* **2010**, *88 (E-supplement 2)*, 826.
12. Croney, C. Should animal welfare policy be affected by consumer perceptions? In *Facing the Challenges of Modern Dairying*; Western Canadian Dairy Seminar, Red Deer, Canada, 2011.
13. Walsh, B. *Time* **2009**, *174*, 30–37.
14. Yiridoe, E. C.; Bonti-Ankomah, S.; Martina, R. C. *Renewable. Agric. Food Syst.* **2005**, *20*, 193–205.
15. Food and Agriculture Organization of the United Nations. *Livestock's Long Shadow - Environmental Issues and Options*; FAO: Rome, 2006.
16. Pelletier, N.; Pirog, R.; Rasmussen, R. *Agric. Syst.* **2010**, *103*, 380–389.
17. Capper, J. L. The environmental impact of conventional, natural and grass-fed beef production systems. In *Proceedings of the Greenhouse Gases and Animal Agriculture Conference 2010*, Banff, Canada, 2010.
18. USDA/NASS. *Livestock Slaughter Annual Summary*; USDA: Washington, DC, 2010.
19. International Trade Centre UNCTAD/WTO Research Institute of Organic Agriculture (FiBL). *Organic Farming and Climate Change*; ITC: Geneva, Switzerland, 2007.
20. IPCC. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; IPCC Secretariat: Geneva, 2007.
21. Strid Eriksson, I; Elmquist, H.; Stern, S.; Nybrant, T. *Int. J. LCA* **2005**, *10*, (Analysis of Pig Production - The Impact of Feed Choice (12 pp). Int. J LCA. 10 LCA (2) 143-154. - Sweden), 143-154.
22. de Vries, A.; de Boer, I. J. M. *Livest. Sci.* **2010**, *128*, 1–11.
23. Vergé, X. P. C.; Dyer, J. A.; Desjardins, R. L.; Worth, D. *Livest. Sci.* **2009**, *121*, 92–101.
24. Pelletier, N. *Agric. Sys.* **2008**, *98*, 67–73.
25. Katajajuuri, J. M. Experiences and improvement possibilities - LCA case study of broiler chicken production. In *Proceedings of the 6th International Conference on Life Cycle Assessment in the Agri-Food Sector*, Zurich, Switzerland, 2008.
26. Rischkowsky, B.; Pilling, D. *The State of the World's Animal Genetic Resources for Food and Agriculture*. Commission on Genetic Resources for Food and Agriculture: Rome, Italy, 2007.
27. Konarzewski, M.; Gavin, A.; McDevitt, R.; Wallis, I. R. *Physiol. Biochem. Zool.* **2000**, *73*, 237–248.

28. Schmidt, C. J.; Persia, M. E.; Feierstein, E.; Kingham, B.; Saylor, W. W. *Poult. Sci.* **2009**, *88*, 2610–2619.
29. Havenstein, G. B.; Ferket, P. R.; Qureshi, M. A. *Poult. Sci.* **2003**, *82*, 1500–1508.
30. Gill, M.; Smith, P.; Wilkinson, J. M. *Animal* **2009**, *4*, 323–333.
31. Pollan, M., Farmer in Chief. *New York Times* 10/09/2008, 2008.
32. Innovation Center for U.S. Dairy. *U.S. Dairy Sustainability Commitment Progress Report*; Innovation Center for U.S. Dairy: Rosemont, IL, 2010.
33. Food Sales. http://www.polyfacefarms.com/taste.aspx.
34. Emission Facts: Average Carbon Dioxide Emissions Resulting from Gasoline and Diesel Fuel http://www.epa.gov/oms/climate/420f05001.htm.
35. Beauchemin, K. A.; Janzen, H.; Little, S. M.; McAllister, T. A.; McGinn, S. M. *Agric. Sys.* **2010**, *103*, 371–379.
36. Ogino, A.; Kaku, K.; Osada, T.; Shimada, K. *J. Anim. Sci.* **2004**, *82*, 2115–2122.
37. Peters, G. M.; Rowley, H. V.; Wiedemann, S.; Tucker, R.; Short, M. D.; Schultz, M. S. *Environ. Sci. Technol.* **2010**, *44*, 1327–1332.
38. Cederberg, C.; Persson, M.; Neovius, K.; Molander, S.; Clift, R. *Environ. Sci. Technol.* **2011**, *45*, 1773–1779.
39. U.S. EPA. *Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990-2005. Annex 3: Methodological Descriptions for Additional Source or Sink Categories*; U.S. EPA: Washington, DC, 2007.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Chapter 25

Evaluation of Poultry Litter Fertilization Practices on Greenhouse Gas Emissions

Dexter B. Watts,* H. Allen Torbert, and Thomas R. Way

USDA-ARS National Soil Dynamics Laboratory,
411 S. Donahue Dr., Auburn, AL 36832
***E-mail: Dexter.Watts@ars.usda.gov. Phone: (334) 844-0864.**

Concentrations of greenhouse gases (GHGs) in the atmosphere have been increasing since preindustrial times. Integrating poultry litter use into conservation agricultural systems could be a management practice for sequestering atmospheric carbon (C) in soil. However, consideration for best management practices for this strategy must be taken into account when applying poultry litter to maximize nutrient uptake and prevent gaseous loss in the form of CO_2, CH_4, and N_2O. This review demonstrates the impact of poultry litter application in agricultural systems on C sequestration. An evaluation of how poultry litter application practices affect gaseous flux of CO_2, CH_4, and N_2O is also discussed.

Introduction

Population increases, industrial expansion, and deforestation are believed to have contributed to elevated atmospheric greenhouse gas (GHG) concentrations (*1–3*). Implications that GHGs may have on global warming and local climate shifts have led to increased pressure by Society to minimize atmospheric concentrations of these gases. As a result of these concerns, scientists are also making research efforts to develop and evaluate abatement practices that reduce GHG emissions.

Greenhouse gases naturally keep the Earth warm by trapping heat in the atmosphere; thus increases in atmospheric concentrations of these gases are predicted to cause shifts in the Earth's climate. Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are the major naturally occurring GHGs

Not subject to U.S. Copyright. Published 2011 by American Chemical Society
In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

responsible for warming the earth while ozone (O_3), water vapor (H_2O), and chlorofluorocarbons (CFCs) are minor contributors. Concentrations of CO_2, CH_4, and N_2O have been increasing at an unprecedented rate, whereas CFCs have leveled off and have started to decline in recent years (*4*). Decreases in CFCs (wholly human-made) are, in part, due to the phasing out of their use.

Presently, CO_2, CH_4, and N_2O are the major GHGs that are of environmental concern prompting interest among the scientific community. Concentrations of these GHGs have been increasing in the Earth's atmosphere since the 1800s, the beginning of the Industrial Revolution. From 1750 to 2005, global concentrations of atmospheric CO_2, CH_4, and N_2O have increased by 36, 148, and 18%, respectively (*4*) and are projected to continually increase in the coming years. For example, the total GHG emissions in the U.S. increased 14% from 1990 to 2008. At the same time, population increased 21% and the country's gross domestic product increased 66%. Changes in emission rates tend to follow population increases, economic development and growth, energy prices and production, seasonal temperature, and technology (*5*).

Agricultural activities can contribute significantly to the GHG global budget. In a recent assessment conducted by the U.S. EPA, in 2008, the Agricultural sector was responsible for emissions of 428 teragrams of CO_2 equivalents (Tg CO_2 Eq.), or 6 percent of total U.S. greenhouse gas emissions. Methane (CH_4) and nitrous oxide (N_2O) were the primary greenhouse gases emitted by agricultural activities. Methane emissions from enteric fermentation and manure management represent about 25 percent and 8 percent of total CH_4 emissions from anthropogenic activities, respectively (*5*). On the other hand, agriculture is a minor contributor of CO_2 and evidence indicates that changes in land management practices could increase the soil's capacity to sequester C, thereby reducing atmospheric concentrations of CO_2. It is believed that 10 to 25% of the current U.S. GHG emissions could be offset through the implementation of improved agricultural and forestry practices which include: land conversions, reduced tillage, afforestation, better forest management, better nutrient management, manure management, and bioenergy production (*5*). Thus, to minimize GHG emissions, considerable effort is needed to identify, quantify, and predict which agricultural practices are sources and sinks for GHGs.

Agriculture has the potential to serve as a sink for CO_2 through the net accumulation of soil C (*5*). The terrestrial reservoir contains approximately 1500 Pg C in the form of organic matter (OM). Agricultural land occupies 40% of the land area in the U.S. (*6*) and therefore could either positively or negatively affect the sequestration of C depending on management choices. Agricultural management choices that will sequester C can be achieved through the implementation of practices that reduce soil disturbance, use of crop rotations and cover crops in intensive cropping systems, addition of organic amendments, conservation reserves, and improved fertilization practices (*7*). For instance, Matson et al. (*8*) reported that the conversion of native land to conventional tillage in 1907 resulted in a soil organic carbon (SOC) loss of 47% by the 1950s for the soil in the central U.S. Corn Belt. Implementing reduced tillage practices in the 1970s resulted in regaining approximately 8% of the native SOC by the 1990s. In addition, pasture management systems have the potential to sequester

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

more C in soil compared to cropping systems due to vigorous rooting of perennial grasses and lack of soil disturbance (*9*, *10*). Similarly, the use of manure as a nutrient source may increase C sequestration through the addition of OM to soil, and thus reduce overall GHG emissions from the agricultural sector.

Poultry Production in the U.S.

Manure use as a soil amendment or a nutrient source in conservation agricultural systems has the potential to increase soil OM, thereby sequestering soil C. Poultry litter (PL) could be regarded as one of the most valuable manure sources. For instance, the U.S. poultry industry is the world's largest producer of poultry meat and the second in exportation as well as a major egg producer. It is estimated that the U.S. poultry industry produces approximately 250 million turkeys (Figure 1) and 8.6 billion broilers (Figure 2) generating approximately 12 million Mg of litter each year (*11*). This turkey and broiler litter is a mixture of poultry manure, feed, and organic bedding material such as sawdust or peanut hulls. The bedding (sawdust or peanut hulls) portion of the broiler litter makes the organic waste a highly carbonaceous material. Generally, the top broiler production facilities are located in the Southern U.S., with approximately 59% of the nation's output (Figure 2). Georgia, Arkansas, Alabama, Mississippi, and North Carolina lead the nation in broiler production (*12*). These poultry production operations are also located in areas where soils have been strongly depleted of SOC from more than 200 years of intense row crop agriculture. This suggests that the soils in this region could greatly benefit from PL additions. Use of PL in regions where poultry is produced has been shown to be an economically competitive N source to commercial inorganic fertilizers (*13*). In other words, PL can serve as a relatively inexpensive source of nutrients for row crop production (*14*). The most typical management practice for PL utilization has been land application, as an organic fertilizer, to pastures and some row crops (Figures 3 and 4).

Poultry litter typically contains high levels of plant macronutrients. Concentrations of carbon (C), nitrogen (N), phosphorus (P), and potassium (K) within PL range between 280 and 300 g kg^{-1}, 39 and 49 g kg^{-1}, 3.6 and 9.9 g kg^{-1}, and 19 and 20 g kg^{-1}, respectively (*15–20*). Poultry litter and other manure sources generally have a long residence life in soil, providing nutrients to crops for several years. From an organic N standpoint, N availability is a function of the decomposition rate. Poultry manure has an organic N availability rate of 55%, broiler litter 55%, swine 40%, cattle feedlot manure 30%, composted cattle feedlot manure 18%, and dairy 21% during the first year after application with the rest of the N becoming available in succeeding years. For example, organic N availability in year two has been reported to be 2% for poultry manure, 5% for broiler litter, 2% for swine, 15% for cattle feedlot manure, 8% for composted cattle feedlot manure, and 14% for dairy (*21*). Similar to N availability of manure, the C added to the soil is released from the soil at a slow rate over time. Likewise, C added with manure will also have an extended life cycle when added to soil.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Thus, management practices that constantly add or retain the C added to soil from manure sources are needed to promote long-term sequestration of C.

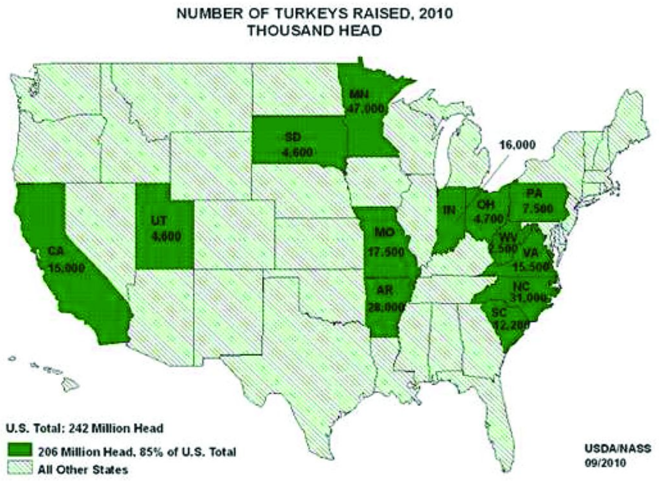

NUMBER OF TURKEYS RAISED, 2010
THOUSAND HEAD
MN 47,000
SD 4,600
16,000
UT 4,600
CA 15,000
MO 17,500
AR 28,000
IN
OH 4,700
PA 7,500
WV 2,500
VA 15,500
NC 31,000
SC 12,200
U.S. Total: 242 Million Head
🟩 206 Million Head, 85% of U.S. Total
▨ All Other States
USDA/NASS
09/2010

Figure 1. Turkey production in the U.S. during 2010 (11).

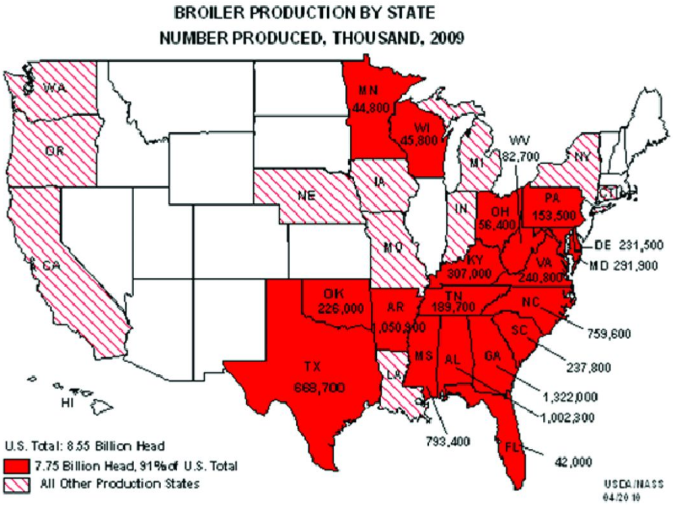

BROILER PRODUCTION BY STATE
NUMBER PRODUCED, THOUSAND, 2009
WA
OR
CA
MN 44,800
WI 45,800
MI
WV 82,700
NY
NE
IA
IN
MO
CT
OH 56,400
PA 153,500
DE 231,500
MD 291,900
KY 307,000
VA 240,800
OK 226,000
AR 1,050,900
TN 189,700
NC
759,600
SC
237,800
MS
AL
GA
1,322,000
1,002,300
LA
TX 668,700
HI
793,400
FL
42,000
U.S. Total: 8.55 Billion Head
🟥 7.75 Billion Head, 91% of U.S. Total
▨ All Other Production States
USDA/NASS
04/2010

Figure 2. Broiler production in the U.S. during 2009 (11).

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

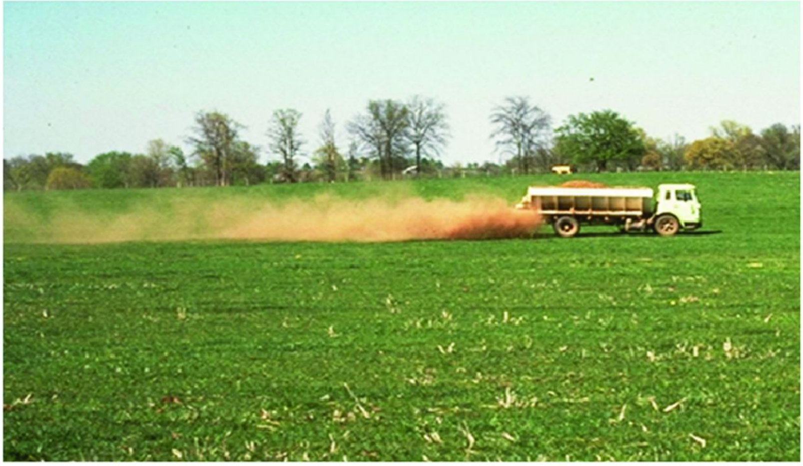


Figure 3. Surface broadcast application of poultry litter to a pasture using a broiler litter spreader truck.

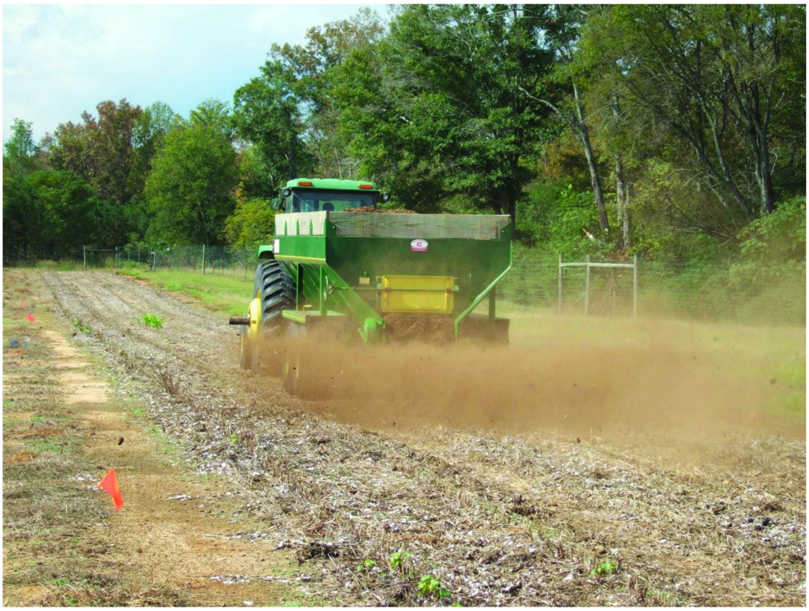


Figure 4. Surface broadcast application of poultry litter to soil using a pull-type litter spreader.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Soil Carbon Sequestration from Poultry Litter Application

Soil C sequestration can be defined as the process of removing atmospheric CO_2 through plant photosynthesis and storing the fixed C in the form of soil OM. For agricultural C sequestration practices to be effective, a new equilibrium within the C cycle must be achieved for which soil C storage outpaces losses to the atmosphere. Soil C concentrations vary from less than 0.5% in sandy Southeastern U.S. soils to greater than 20% in wetlands and bogs. Cultivated soils often range from 0.5% to 3% C (*22*).

Although C storage deep within the ocean floor is considered to be one of the major reservoirs, manipulating this pool to increase sequestration could take millions of years. Also, our ability to influence this pool is limited. The SOC pool is the second largest reservoir and is presently the easiest to manipulate (*22*).

Dramatic changes in soil have occurred, starting during the beginning of 20th century when agriculture promoted rapid soil C losses. Changes in agricultural practices could recover much of this C loss. For instance, a net carbon sequestration of approximately 14% of the U.S. total CO_2 emissions in 2008 was achieved through land-use and forestry related activities. Carbon sequestration from land use change and forestry was more than 13% from 1990 to 2008. Although most of this C was sequestered within trees in forestry, U.S. crops and animal manure management practices have the potential to sequester C in crop and pasture systems. It is estimated that in 2008, forest ecosystems (comprised of vegetation, soils, and harvested wood) were responsible for 84% of total net CO_2 flux, urban trees accounted for 10%, changes in mineral and organic soil carbon pools accounted for 5%, and landfilled yard trimmings and food scraps accounted for 1%. Sequestration within forest systems was a result of forest growth and increased forested area, as well as a net accumulation of carbon stored within the harvested wood. Sequestration within urban forest resulted from net tree growth within these areas. Mineral and organic agricultural soils sequester approximately 5.9 times as much C as is emitted from soils that are limed and use urea fertilization (*5*). Carbon sequestration within mineral soils has primarily resulted from conversion of cropland to permanent pastures and hay production systems, a reduction in summer fallow areas in semi-arid areas, increased adoption of conservation tillage system practices, and greater use of organic fertilizers (i.e., manure and sewage sludge) applied to agriculture lands. These practices offset approximately 16% of total U.S. CO_2 emissions, or 14% of total greenhouse gas emissions in 2008. From 1990 to 2008, land-use change and forestry net C loss resulted in a 3.4% increase in CO_2 sequestration. This was primarily due to increases in net C accumulation from forest C stocks, predominantly tree biomass, and harvested wood (*5*).

Commercial fertilizer and manure use in agricultural systems have the potential to increase soil C sequestration through the increase in plant production and crop residue added to soil. Franzluebbers (*23*) estimated the net C sequestration potential of cropping systems that used N fertilizer. Franzluebbers used a dataset from six literature sources of various crops grown on southeastern U.S. soils and reported that net C sequestration could be optimized at 0.24 Mg C ha^{-1} yr^{-1} with application rates of 108 kg N ha^{-1} yr^{-1}. This calculation took into

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

account a cost of 1.23 kg C kg^{-1} N for production, manufacturing, distribution, and application (*24*). Also, with the assumption that N fertilizer application would contribute to N_2O flux, which was 296 times the CO_2 global warming potential (*25*), net C offset from fertilization would be maximized at 0.07 Mg C ha^{-1} yr^{-1} with an application rate of 24 kg N ha^{-1} yr^{-1}. Regarding mitigating GHG emissions, their calculations suggest a positive, but diminishing return with increasing fertilizer N application (*10*).

Addition of nutrients to the soil in the form of animal manures such as PL could have an even greater impact on C sequestration compared to inorganic fertilizer sources. Poultry litter additions could be a valuable resource for agricultural soils if utilized correctly for production and C sequestration in the southeastern U.S. It was suggested by Nyakatawa et al. (*26*) that PL additions to cropping systems with annual winter crops could be an environmentally friendly management practice that would reduce the reliance on commercial fertilizers. Endale et al. (*27*) reported that the addition of PL in a no-tillage system produced 50% greater cotton lint (*Gossypium hirsutum* L.) than conventionally tilled and fertilized cotton in the Southern Piedmont region. Parker et al. (*28*) found 7 to 20% greater SOC in the surface 5 cm of soil under a cotton-rye cropping system with PL compared to commercial fertilizer in the Tennessee Valley after 5 years. Sainju et al. (*29*) found an 18% increase in SOC under a no tillage (NT) cotton system using PL (100 kg available N ha^{-1}) compared to a NH_4NO_3 (100 kg N ha^{-1}) system in the surface 10 cm of soil after 10 years. Watts et al. (*30*) reported a 65% increase in SOC under a NT corn (*Zea mays* L.) system using PL (170 kg total N ha^{-1}) compared to NH_4NO_3 (170 kg N ha^{-1}) in the surface 0-5 cm of soil after 14 years of management.

Franzluebbers (*23*) evaluated the impact of PL application to crop and pasture land in studies separated into a dataset of two-year studies and a dataset of studies greater than two years. Using a total of 19 comparisons, SOC was 11% greater with PL applications compared to without PL. When comparisons were made among the studies greater than two years, SOC was 20% greater than soils without litter application. Soil C sequestering increased 0.26±2.15 Mg ha^{-1} yr^{-1} among all 19 comparisons of studies with less than two years with manure application compared to soils without manure. When comparing soil with greater than two years of application, soils with manure were 0.72 ±0.67 Mg ha^{-1} greater than soils without manure. When converting the increase in C sequestration resulting from PL additions to a percentage, SOC was increased 17±15%. It was also reported by Franzluebbers (*23*) that SOC accumulation rates from manure land application in other parts of the world include 0.10-0.23 Mg ha^{-1} yr^{-1} during 18 years in Kenya (*31*), 0.15 Mg ha^{-1} yr^{-1} during 60 years in Denmark (*32*), 0.20 Mg ha^{-1} yr^{-1} during 22 years in Italy (*33*), 0.20-0.22 Mg ha^{-1} yr^{-1} during 45 years in Nigeria (*34*), 0.21-0.54 Mg ha^{-1} yr^{-1} during 20 years in India (*35*), 0.50 Mg ha^{-1} yr^{-1} during 135 years in England (*36*), and 1.02 Mg ha^{-1} yr^{-1}during 4 years in England (*37*). Franzluebbers (*23*) concluded that the SOC sequestration rates from PL in the southeastern U.S. are within the upper range reported by other studies around the world. Some of the divergence may have been due to differences in animal manure sources (typically cattle manure was used in other parts of the world) and length of study investigations.

Contribution of Poultry Litter to GHG Emissions

Carbon Dioxide Emissions

Carbon dioxide loss from agricultural soil is primarily through the process of OM decomposition. Autotrophic microbes are the engines that drive this process. Soil microbes use photosynthetically fixed C found in OM as a food source to grow in the presence of oxygen, with the end result of this respiration being CO_2 release. The following discussion evaluates the impact of PL application on soil loss of CO_2 from different agricultural management practices.

In a study comparing the effects of PL addition to different tillage (NT- no tillage; CT- conventional tillage; and MT-mulch tillage) on CO_2 loss from soil under a cotton production system, Roberson et al. (*38*) found that CT with PL (100 kg available N ha^{-1}) produced the greatest CO_2 loss, while NT with NH_4NO_3 at 100 kg N ha^{-1} generated the lowest CO_2 loss. All tillage practices with PL produced higher CO_2 fluxes compared to treatments with NH_4NO_3 at the same rate. Roberson et al. (*38*) reported that this was to be expected because the PL additions resulted in larger C inputs to soil. Approximately 1.2, 1.4, and 3.2 t ha^{-1} of organic C was added to soil from PL (100 kg N ha^{-1}) additions in 2003, 2004, and 2006, respectively. When comparing the PL only treatments, CT and MT resulted in higher CO_2 fluxes throughout the growing season compared to NT (*38*). This suggests that the addition of PL to soil under high intensity tillage practices, which produces greater soil disturbance, results in higher CO_2 loss. Losses were in the order of CT > MT > NT. This indicates that increased tillage increases soil aeration thereby increasing exposure of soil microbes to soil C. Roberson et al. (*38*) reported that CT and MT with 100 kg N ha^{-1} PL released 27% and 25% more CO_2 into the atmosphere, respectively, compared to NT at the same rate of PL. Higher CO_2 flux was observed with 200 kg ha^{-1} of PL compared to 100 kg ha^{-1} when applied to soil. On average, plots receiving PL at 100 and 200 kg N ha^{-1} had 24% and 26% higher CO_2 fluxes, respectively, compared to 100 kg N ha^{-1} NH_4NO_3.

Poultry litter addition to soil at different compaction levels has also been shown to impact CO_2 loss. Pengthamkeerati et al. (*39*) evaluated CO_2 loss from soil at bulk densities of 1.2, 1.4 1.6, and 1.8 Mg m^{-3} with and without PL (0 and 19 Mg ha^{-1}). Soil CO_2 fluxes decreased with increasing bulk densities in both the PL amended and non-amended soil. Compared to the lowest bulk density (1.2 Mg m^{-3}), as bulk density increased, soil CO_2 fluxes decreased between 18-72% and 5-69% for litter amended and unamended soil, respectively (*38*).

Jones et al. (*40*) evaluated the impact of annual CO_2-C loss in a temperate Italian ryegrass (*Lolium perenne*) grassland during two growing seasons fertilized with NH_4NO_3, sludge pellets, cattle slurry, and PL applied at a rate of 300 kg N ha^{-1}. Annual CO_2-C loss was in the order of 17.22 > 14.03 > 13.99 > 10.44 tonnes ha^{-1} for PL, cattle slurry, sludge pellets, and NH_4NO_3, respectively during 2002. The manure C content in 2002 was in the order of 17.13 > 16.79 > 6.93 > 0 for sludge pellets, PL, cattle slurry, and NH_4NO_3, respectively. The estimated manure C remaining (sequestered) in soil at 2002 year end was in the order of 13.59 > 10.02 > 3.34 tonnes ha^{-1} for sludge pellets, PL, cattle slurry, and NH_4NO_3, respectively. Annual CO_2-C loss during 2003 was in the order of 17.22 > 15.89

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

> 15.47 > 11.79 tonnes ha^{-1} for PL, cattle slurry, sludge pellets, and NH_4NO_3, respectively. The manure C content in 2003 was in the order of 17.13 > 16.79 > 5.02 > 0 for sludge pellets, PL, cattle slurry, and NH_4NO_3, respectively. The estimated manure C remaining (sequestered) in soil at 2003 year end was in the order of 13.46 > 11.36 > 0.92 > 0 tonnes ha^{-1} for sludge pellets, PL, cattle slurry, and NH_4NO_3, respectively. This study shows that although more CO_2 may be lost from manure nutrient sources, these organic sources have a greater chance of sequestering C compared to inorganic N. These results also show that of the manure nutrients, the dry sources have a greater potential for C sequestration. Jones et al. (*40*) also reported that manure additions to grasslands plots resulted in greater C sequestration potential after 6 years despite an increase in CO_2 flux. However, manure's ability to sequester C was variable, with the greatest amount of the C retained with poultry manure and the least with sewage sludge.

Manure incorporation through tillage is a management practice that is commonly used to reduce nutrient losses from agricultural fields utilizing manure as fertilizers. Few studies have been conducted to evaluate gaseous losses from this management practice. Comparing the impact of subsurface application vs. surface application of PL, Watts et al. (*41*) evaluated CO_2 loss from surface broadcasted PL, subsurface banded PL at 25 cm band spacings, subsurface banded PL at 38 cm spacings, surface broadcasted urea, and a nonfertilized control in bermudagrass pastures (*Cynodon dactylon* L.). All nutrient sources were applied at a rate of 330 kg total N ha^{-1}. Subsurface banded PL was applied in a trench 4 cm wide, 5 to 8 cm below the soil surface using a prototype implement that backfilled soil on top of the banded PL (Figures 5 and 6). Monitoring of CO_2 emissions showed that the greatest loss was observed when PL was applied in subsurface bands spaced 25 cm apart and the lowest loss was observed in the control and urea treatments. Watts et al. (*41*) attributed the higher CO_2 loss from the 25 cm banded treatments to greater soil disturbance resulting from PL subsurface application. A comparison of the PL treatments showed that CO_2 loss from soil was in the order of subsurface banded PL at 25 cm spacing > surface broadcast > subsurface banded at 38 cm spacing. This suggests that as the subsurface band spacing increases, the potential for CO_2 loss decreases. These results therefore suggest that subsurface banding PL in soil shows promise for reducing CO_2 loss if the correct banding spacing is applied.

Methane Emissions

Methane emission from soil occurs during the terminal stages of anaerobic decomposition of OM. Generally, soil functions as a small consumer of methane. In most instances, when a soil environment is conducive for methane production, flooded conditions in association with high levels of organic substance are usually present. Most of the past research on methane production from agricultural systems using manure sources has been with liquid manure or under flooded fields. There is a scarcity of research on the impacts that PL contributes to methane production in agricultural systems, particularly because PL is generally a dry material.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

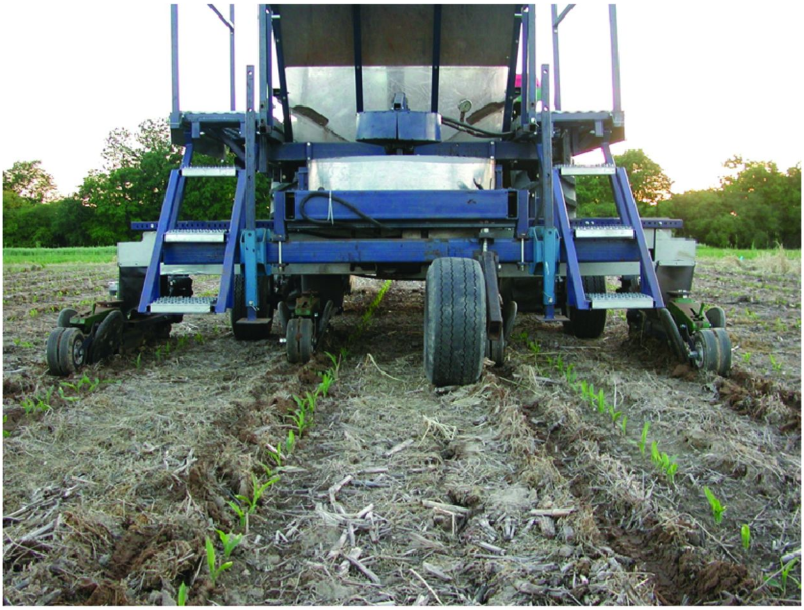


Figure 5. Rear view after subsurface band application of poultry litter using a four-row prototype banding implement.

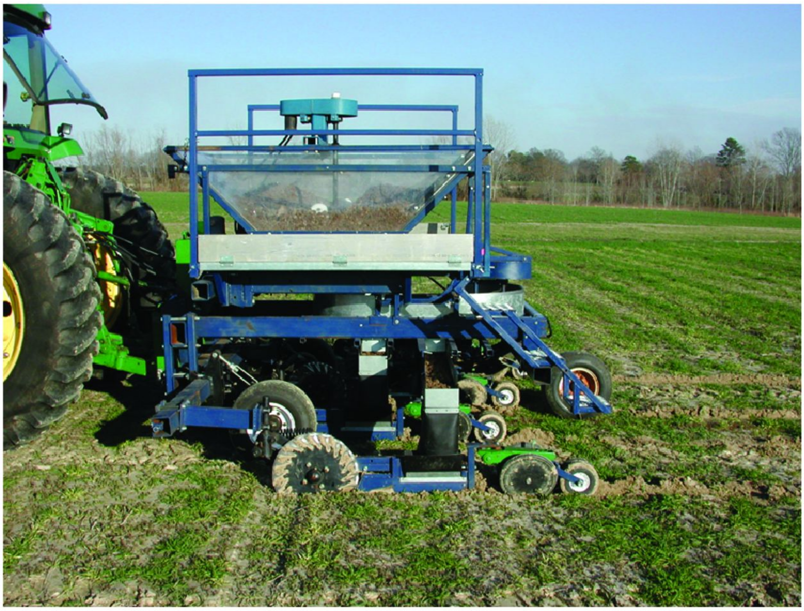


Figure 6. Side view after subsurface band application of poultry litter using the four-row prototype banding implement shown in Figure 5. Direction of forward travel is from right to left.

Jones et al. (*42*) evaluated the impact of methane production from a control (nonfertilized), NH_4NO_3, urea, cattle slurry, sewage sludge pellets, and PL additions to ryegrass grassland used for silage. The N sources were applied at a rate of 300 kg available N ha^{-1}. Cattle slurry was the only organic fertilizer source that significantly increased CH_4 production. Methane fluxes from PL additions were not significantly different from the control.

Chadwick et al. (*43*) evaluated pig slurry, dilute dairy cow effluent, pig farm yard manure, beef farm yard manure, layer manure, and control. Methane flux was the greatest with dairy cow slurry followed by pig slurry compared to the other manure sources. Layer manure emissions were lower compared to the other manure sources. Chadwick et al. (*43*) reported that more than 90% of the total CH_4 fluxes occurred during the first 24 hr after applying the slurry manure sources. They attributed this methane loss to greater volatilization of dissolved CH_4 and through the production of volatile fatty acids (C_2-C_5) present in the manures. Thus, CH_4 flux emitted into the atmosphere was primarily a result of the slurry and not the soil. Thus, liquid manure sources provide readily oxidizable C to activate the population of methanotrophs under conditions where oxygen is limited. The same may be true for solid manures (*44*).

In evaluating the impact of subsurface application vs. surface application of PL to bermudagrass pasture, Watts et al. (*41*) monitored CH_4 loss of surface broadcasted PL, subsurface banded PL at 25 cm spacings, subsurface banded PL at 38 cm spacings, urea applied at a rate of 330 kg total N ha^{-1}, and a nonfertilized control. The different fertilizer sources and application methods were evaluated for 44 days. Generally, CH_4 flux was low throughout most of the sampling period. Subsurface banding PL tended to increase CH_4 flux in soil compared to surface application practices. This was most evident on days following rainfall events. The greatest flux was observed for the 38 cm band spacing. This was probably because there is greater distance between bands, so there was more PL concentrated within each band, compared to the 25 cm band spacing. Methane flux was greatest when PL was applied using the 38 cm band spacing.

Nitrous Oxide Emissions

Nitrous oxide flux from agricultural soil is lost as a result of microbial transformations via the nitrification or denitrification process. Nitrification and denitrification often occur simultaneously when associated with N fertilization. Oxygen availability in soil is the most important factor regulating nitrification and denitrification release of N_2O. In well aerated soil environments, nitrification is normally correlated with NH_4 concentrations and not as much with NO_3. Dentrification primarily occurs under anaerobic environments; however some denitrifying microorganisms are able to produce N_2O under aerobic conditions where oxygen is limited. Conversely, nitrification occurs only under strictly aerobic conditions since enzymes of nitrifying organisms require O_2 for activation during the NH_4 oxidation process (*45*). In the following section, N_2O flux from various soil environments is discussed; however the authors do not discern whether N_2O flux was a result of nitrification or denitrification.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Gaseous loss of N from manure and urea-based fertilizers primarily occurs as NH_3 or N_2O. Cumulative N loss from NH_3 volatilization can amount to a significant portion of the N applied. Ammonia volatilization losses from broiler litter have been found to range from 4 to 60% of N applied in a laboratory study (*46–48*). Some field studies on surface applied poultry wastes have reported total losses of < 7% of total applied N (*49*, *50*), while others have reported up to 24% (*51*). Similar losses have been observed with other animal waste (*52–54*). In a review paper, Colbourn and Dowdell (*55*) concluded that denitrification losses of inorganic N range between 0 - 20% of N applied to arable soils and 0 - 7% on grassland soils. Nitrous oxide losses of 11 to 37% of total N applied have been reported from forage systems amended with dairy manure in the southeastern U.S. (*56*). However, these N_2O losses are much higher than the Intergovernmental Panel on Climate Change (IPCC)-estimated losses of an average 1.25% (ranging from 0.25 to 2.25%) for commercial fertilizer and manure (*57*). Nitrous oxide losses from broiler litter ranged from 0 - 3.7% of applied N after five months under laboratory aerobic incubations (*58*). In a study that attributed most of the N_2O loss to dentrification, flux of N_2O from plots treated with fresh broiler litter was 3.87 kg ha^{-1} which represented a loss of 1% of total N applied (*59*). Eichner (*60*) estimated that 2% of N from fertilizer is lost as N_2O over a one year period in fertilized and manured soils. Estimates of worldwide N use efficiency are about 30 to 50% in most agricultural soils, subjecting the excess to gaseous loss, leaching or runoff (*61*). From an agricultural management standpoint, 1 - 2% of N loss as N_2O seems insignificant; however from a global warming perspective, this loss could be substantial. In succeeding text, the contribution of different poultry litter application management practices to N_2O loss is discussed.

Thornton et al. (*59*) evaluated the impact of a control (nonfertilized check), urea, composted PL, and fresh PL on N_2O loss in a bermudagrass pasture using an automated measuring system. This system was able to analyze experimental plots every three hours for a total of 8 complete gas flux measurements per day. The N sources were surface applied at a rate of 336 kg available N ha^{-1} split into four applications approximately six weeks apart. Following June fertilization, emissions were relatively low during the first and second week after application when the soil water-filled pore space decreased from 72% on the day of application to 49%. During this time, urea was the largest N_2O emitter. Within 2-3 hr after 17 mm of rainfall, a spike in N_2O flux was observed from all N-treated plots. However, N_2O emissions from the control plots following rainfall were relatively the same as prior to the rainfall event. Nitrous oxide flux from the fresh PL was most pronounced following the first rainfall event after application. During other rainfall events, N_2O fluxes were observed, however they were less prominent. The pattern where urea was the largest emitter prior to rainfall events and fresh PL was the greatest emitter after rainfall events was observed during every wetting and drying cycle. The magnitudes of emissions tended to depend on soil moisture. Cumulative N losses as N_2O for the 135 days of evaluation were in the order of 3.87 kg ha^{-1} in fresh PL plots, 2.96 kg ha^{-1} in urea plots, 1.64 kg ha^{-1} in composted PL plots, and 0.51 kg ha^{-1} in the control plots. When comparing the effect of 336 kg of available N ha^{-1} on N_2O flux, fresh PL lost approximately 1%, urea lost 0.73%, and composted PL lost approximately 0.32% of the N applied.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Marshall et al. (*62*) evaluated N balance in three soil types from different Regions in the Southeastern U.S. (Cumberland Plateau, Piedmont, and Coastal Plain). Broiler litter was applied to tall fescue (*Festuca arundinacea* Schreb.) pasture at a rate of 70 kg of available N ha^{-1}. Approximately 6% of the N was lost through ammonia volatilization and denitrification. Ammonia volatilization losses were in the order of 3.25% for Coastal Plain, 5.25% for Piedmont, and 2.55% for Cumberland Plateau. Nitrate leaching appeared to be significant only in the Coastal Plain soil. This was most likely a result of the soil's sandy nature. Nitrous oxide loss from soil was 3.34% in the Coastal Plain, 1.6% in the Piedmont, and 0.61% in the Cumberland Plateau. Plant uptake represented approximately 43%. These losses are similar to other findings in the literature. Chang et al. (*63*) observed that denitrification losses from manured soil accounted for approximately 2-4% of the applied N. Ryden (*64*) found that denitrification loss to be as much as 5% of the N applied to grassland soils. Marshall et al. (*62*) concluded, from the study evaluating nitrogen budget (all N pathways) of fescue pastures fertilized with broiler litter on three major soil types in the Southeastern U.S., that N_2O emission was not the major pathway for N loss. They also suggested that better nutrient management practices such as fertilization timing and placement are needed to supply the optimal amounts of N for crop uptake while minimizing N loss through gaseous forms.

Akiyama and Tsuruta (*65*) evaluated N_2O loss from an agricultural field used to grow Pac choi (*Brassica* spp.). Nitrous oxide measurements were collected six times a day using automated equipment. The N sources were urea, swine manure (composted and dried), and poultry manure (with no bedding dried and granulated). Manure sources were surface broadcasted and then incorporated. The N sources were applied at a rate of 15 g N m^{-2}. Nitrous oxide measurements were evaluated for an entire year. Pac choi was cultivated two months after fertilization and plots were left fallow the remainder of the year. Akiyama and Tsuruta (*65*) reported that during the cultivation period, the total N_2O emissions from poultry manure (no bedding) and swine manure-amended plots were 592% and 163%, respectively, of that from urea-amended plots. They speculated that manure application resulted in development of anaerobic microsites in soil, which most likely enhanced dentrification. Total N_2O fluxes for the year for poultry manure, swine manure, and urea were 184, 61.3 and 44.8 mg N m^{-2}, respectively. The Pac choi recovered 54.5 to 66.3% of the N applied and N_2O accounted for 0.47 to 1.23%, suggesting that the remainder was lost due to leaching or NH_3 volatilization.

In a bermudagrass pasture fertilized with turkey litter, Sauer et al. (*66*) reported that in 2000 and 2001, magnitudes of annual cumulative N_2O fluxes were 1.59 and 0.98 kg N ha^{-1}, respectively, corresponding to 0.74 and 1.34% of the turkey litter N applied each year. Cumulative seasonal N_2O emission increased 50% as a response to turkey-litter additions compared to nonfertilized controls. Interseeding rye into the bermudagrass pasture resulted in a four-fold reduction in N_2O flux compared to with no rye. This was because the interseeded rye was capable of utilizing soil NO_3 that had mineralized from the turkey litter during periods when the bermudagrass was dormant, and thus minimized the susceptibility for N_2O production.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Coyne et al. (*67*) investigated N_2O flux from grass strips used as buffers to control erosion from chisel tillage plots fertilized with PL applied at a 16.5 Mg ha^{-1} (wet wt.). They observed lower N_2O loss from grass filters receiving runoff from PL amended soil compared to plots where manure was directly applied to soil. While populations of denitrifying bacteria (100-fold greater) were higher in the grass filters, the erosion plots (tilled plot where PL was applied) had greater soil NO_3 levels which contributed to greater denitrification, permitting more N_2O to be lost to the atmosphere. Coyne et al. (*68*) also reported that following rainfall simulation, N_2O loss was greater in grass buffer strips receiving runoff, compared to buffer strips not receiving runoff. N_2O emissions were greater in buffer strips that abutted manured plots and decreased as the distance from the manured plots increased.

In a study by Jones et al. (*61*) where NH_4NO_3, urea, cattle slurry, broiler litter, and sludge pellets were applied at a rate of 300 kg available N ha^{-1} in a temperate grassland in the UK, higher N_2O flux was observed with the use of organic fertilizers compared to the commercial fertilizer sources. Losses of N_2O were in the order of sludge pellets > broiler litter > cattle slurry > NH_4NO_3 > urea. Nitrous oxide flux from manured treatments extended for longer periods of time and was greater in magnitude than for unmanured treatments. Jones et al. (*69*) attributed higher N_2O fluxes in soil under manured treatments to greater inputs of total N, providing additional mineralized N over longer periods of time. The average N_2O flux observed for 2002 and 2003 corresponded to 0.75% of the N applied for NH_4NO_3, 0.25% for urea, 2.8% for sludge pellets, 0.35% for cattle slurry, and 1.55% for broiler litter. Residual effects (no fertilizer was applied) were observed in the manured treatment in 2004, producing significantly higher N_2O flux than in 2002 and 2003.

To assess the impact of subsurface application vs. surface application of PL on N_2O emissions, Watts et al. (*41*) measured N_2O losses from surface broadcasted PL, subsurface banded PL at 25 cm spacings, subsurface banded PL at 38 cm spacings, urea, and a nonfertilized control. All nutrient sources were applied at a rate of 330 kg total N ha^{-1}. Subsurface applying PL at 5 to 8 cm below the soil surface in bands spaced 38 cm apart resulted in the greatest N_2O loss. The lowest loss was observed in the control. Watts et al. (*41*) attributed the higher N_2O flux from the 38 cm banded treatments to a greater concentration of PL within the individual subsurface bands. Also, once a rainfall event had occurred, the moisture within the bands became elevated and retained for prolonged periods of time compared to surface applied treatments due to the restricted aeration within bands. A comparison of the PL treatments only showed that N_2O loss from soil was in the order of subsurface banded PL at 38 cm spacing > subsurface banded at 25 cm spacings > surface broadcast. The results suggest that as distance between subsurface band increases, the potential for N_2O loss increases. On the other hand, applying PL in subsurface bands spaced closer together has a lower potential for N_2O loss. These results showed that subsurface banding PL in soil has promise for reducing N_2O loss if the correct banding spacing is applied.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Conclusion

Concentrations of greenhouse gases CO_2, CH_4 and N_2O in the atmosphere have increased at an unprecedented rate since the beginning of the Industrial Revolution. Agriculture has the potential to sequester and reduce atmospheric concentrations of these gases through management and land use change. Thus, knowledge of soil C and N dynamics is key to wise land use management, which is also integral to sustaining our fertile agricultural lands and increasing their productivity. This review evaluated how poultry litter application practices are used in agricultural systems to increase SOC buildup. To determined the stability of poultry litter C additions to soil, more long-term studies are needed. Several studies have demonstrated how different poultry litter application practices can impact CO_2, CH_4, and N_2O fluxes, suggesting that careful management must be taken into account when applying poultry litter to agricultural soils. This review focused primarily on direct measurements from poultry litter applications taken from agricultural fields. Future studies are needed to evaluate indirect measurements because N and C losses downstream with surface water runoff or through leaching could also contribute to GHG emissions. Agriculture has the potential to reduce GHG emissions through the use of organic amendments such as poultry litter, however considerable effort is needed to better indentify, quantify, and predict which agricultural practices are sources and sinks for GHGs in order to minimize greenhouse gas losses from agricultural systems.

References

1. Holland, H. D. *The chemistry of the atmosphere and oceans*; John Wiley and Sons: New York, 1978.
2. Smil, V. *Carbon nitrogen sulfur: Human interference in grand biospheric cycles*; Plenum Press: New York, 1985.
3. Warneck, P. *Chemistry of the natural atmosphere*; Academic Press: London, 1988.
4. Intergovernmental Panel on Climate Change. *The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor M., Miller, H. L., Eds.; Cambridge University Press; Cambridge, U. K., 2007.
5. U.S. Environmental Protection Agency. *Inventory of U.S. greenhouse gas emissions and sinks: 1990-2008*; EPA, Office of Atmospheric Programs (6207J): Washington, DC, 2010. URL http://epa.gov/climatechange/emissions/usinventoryreport.html (Accessed 18 May 2010; verified 18 May 2010).
6. Nation's Encyclopedia. *United States of America Agriculture*; 2007; URL http://www.nationsencyclopedia.com/economies/Americas/United-States-of-America-AGRICULTURE. (Accessed Nov. 16, 2010).

7. Lokupitiya, E.; Paustian, K. Agricultural soil greenhouse gas emissions: A review of national inventory methods. *J. Environ. Qual.* **2006**, *35*, 1413–1427.
8. Matson, P. A.; Parton, W. J.; Power, A. G.; Swift, M. J. Agricultural Intensification and Ecosystem Properties. *Science* **1997**, *277*, 504–509.
9. Follett, R. F.; Kimble, J. M.; Lal, R. *The potential of U.S. grazing lands to sequester carbon and mitigate the greenhouse effect*; Lewis Publ: Boca Raton, FL. 2001
10. Causarano, H. J.; Franzluebbers, A. J.; Reeves, D. W.; Shaw, J. N. Soil organic carbon sequestration in cotton production systems of the Southeastern United States: A Review. *J. Environ. Qual.* **2006**, *35*, 1374–1383.
11. USDA National Agricultural Statistics Service. *Poultry, Charts and Maps*; URL http://www.nass.usda.gov/Charts_and_Maps/Poultry/index.asp (Accessed June 17, 2011).
12. Reddy, K. C.; Reddy, S. S.; Malik, R. K.; Lemunyon, J. L.; Reeves, D. W. Effect of five-year continuous poultry litter use in cotton production on major soil nutrients. *Agron. J.* **2008**, *100*, 1047–1055.
13. Chapman, S. L. Soil and solid poultry waste nutrient management and water quality. *Poult. Sci.* **1996**, *75*, 862–866.
14. Nyakatawa, E. Z.; Reddy, K. C. *Conservation tillage and poultry litter effects on cotton and corn yields: Five year results*; van Santen, E., Ed.; Proc. Annu. Southern Conservation Tillage Conf. for Sustainable Agriculture, 25th, Auburn, AL, 24–26 June 2002; pp 142–147.
15. Sims, J. T. Nitrogen transformations in a poultry manure amended soil: temperature and moisture effects. *J. Environ. Qual.* **1986**, *15*, 59–63.
16. Kingery, W. L.; Wood, C. W.; Delaney, D. P.; Williams, J. C.; Mullins, G. L. Impact of long-term land application of broiler litter on environmentally related soil properties. *J. Environ. Qual.* **1994**, *23*, 139–147.
17. Williams, C. M.; Barker, J. C.; Sims, J. T. Management and utilization of poultry wastes. *Rev. Environ. Contam. Toxicol.* **1999**, *162*, 105–157.
18. Ekinci, K.; Keener, H. M.; Elwell, D. L. Compositing short paper fiber with broiler litter and additives. Part 1. Effects of initial pH and carbon/nitrogen ratio on ammonia emission. *Compost Sci. Util.* **2000**, *8*, 160–172.
19. Sauer, T. J.; Daniel, T. C.; Nichols, D. J.; West, C. P.; Moore, P. A.; Wheeler, G. L. Runoff water quality from poultry litter-treated pasture and forest sites. *J. Environ. Qual.* **2000**, *29*, 515–521.
20. Pote, D. H.; Kingery, W. L.; Aiken, G. E.; Han, F. X.; Moore, P. A., Jr.; Buddington, K. Water-quality effects of incorporating poultry litter in perennial grassland soil. *J. Environ. Qual.* **2003**, *32*, 2392–2398.
21. Eghball, B.; Weinhold, B. J; Gilley, J. E; Eigenberg, R. A. Mineralization of manure nutrient. *J. Soil Water Conserv.* **2002**, *57*, 470–473.
22. McVay, K. A.; Rice, C. W. *Soil organic carbon and the global carbon cycle*; Kansas State University Agricultural Experiment Station and Cooperative Extension Service Technical Bulletin; MF-2548; Manhattan, KS, 2002.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

23. Franzluebbers, A. J. Soil organic carbon sequestration and agricultural greenhouse gas emissions in the southeastern U.S. *Soil Tillage Res.* **2005**, *83*, 120–147.
24. Izaurralde, R. C.; McGill, W. B; Bryden, A.; Graham, S.; Ward, M.; Dickey, P. Scientific challenges in developing a plan to predict and verify carbon storage in Canadian Prairie soils; In *Management of carbon sequestration in soil*; Lal, R., Kimble, J. M., Follett, R. F., Stewart, B. A., Eds.; CRC Press: Boca Raton, FL, 1998; pp. 433–446.
25. Intergovernmental Panel on Climate Change. Agriculture: Nitrous oxide from agricultural soils and manure management. In *Guidelines for National Greenhouse Gas Inventories*; Organization for Economic Co-operation and Development: Paris, France, 1997; Chapter 4.
26. Nyakatawa, E. Z.; Reddy, K. C; Brown, G. F. Residual effect of poultry litter applied to cotton in conservation tillage systems on succeeding rye and corn. *Field Crops Res.* **2001**, *71*, 159–171.
27. Endale, D. M.; Cabrera, M. L; Steiner, J. L; Radcliffe, D. E; Vencill, W. K; Schomberg, H. H; Lohr, L. Impact of conservation tillage and nutrient management on soil water and yield of cotton fertilized with poultry litter or ammonium nitrate in the Georgia Piedmont. *Soil Tillage Res.* **2002**, *66*, 55–68.
28. Parker, M. A.; Nyakatawa, E. Z; Reddy, K. C; Reeves, D. W. Soil carbon and nitrogen as influenced by tillage and poultry litter in North Alabama. In *Making conservation tillage conventional: Building a future on 25 years of research*; van Santen, E., Ed.; Proc. 25th Annu. Southern Conserv. Tillage Conf. Sustainable Agric., Auburn, AL, 24–26 June 2002; pp 283–287. URL http://www.ag.auburn.edu/aux/nsdl/sctcsa/sctcsa_2002/docs/proceedings/Parker.pdf (Accessed Feb. 14, 2011).
29. Sainju, U. M.; Senwo, Z. N.; Nyakatawa, E. Z.; Tazisong, I. A.; Reddy, C. Tillage, cropping systems,and nitrogen fertilizer source effects on soil carbon sequestration and fraction. *J. Environ. Qual.* **2008**, *37*, 880–888.
30. Watts, D. B.; Torbert, H. A.; Prior, S. A.; Huluka, G. Long-term tillage and poultry litter impacts on soil carbon and nitrogen mineralization and fertility. *Soil Sci. Soc. Am. J.* **2010**, *74*, 1239–1247.
31. Kapkiyai, J. J.; Karanja, N. K.; Qureshi, J. N.; Smithson, P. C.; Woomer, P. L. Soil organic matter and nutrient dynamics in a Kenyan nitisol under long-term fertilizer and organic input management. *Soil Biol. Biochem.* **1999**, *31*, 1773–1782.
32. Christensen, B. T. Effects of animal manure and mineral fertilizer on the total carbon and nitrogen contents of soil size fraction. *Biol. Fertil. Soils* **1988**, *5*, 304–307.
33. Govi, M.; Francioso, O.; Ciavatta, C.; Sequi, P. Influence of long-term residue and fertilizer applications on soil humic substances: a case study by electrofocusin. *Soil Sci.* **1992**, *154*, 8–13.
34. Agbenin, J. O.; Goladi, J. T. Carbon, nitrogen and phosphorus dynamics under continuous cultivation as influenced by farmyard manure and inorganic fertilizers in the savanna of northern Nigeria. *Agric. Ecosyst. Environ.* **1997**, *63*, 17–24.

35. Gupta, A. P.; Narwal, R. P.; Antil, R. S.; Dev, S. Sustaining soil fertility with organic-C, N, P, and K by using farmyard manure and fertilizer-N in a semiarid zone: a long-term study. *Arid Soil Res. Rehabil.* **1992**, *6*, 243–251.
36. Webster, C. P.; Goulding, K. W. T. Influence of soil carbon content on denitrification from fallow land during autumn. *J. Sci. Food Agric.* **1989**, *49*, 131–142.
37. Bhogal, A.; Shepherd, M. Effect of poultry manure on the leaching of carbon from a sandy soil as a potential substrate for denitrification in the subsoil. *J. Sci. Food Agric.* **1997**, *74*, 313–322.
38. Roberson, T.; Reddy, K. C.; Reddy, S. S.; Nyakatawa, E. Z.; Raper, R. L.; Reeves, D. W.; Lemunyon, J. Carbon dioxide efflux from soil with poultry litter applications in conventional and conservation tillage systems in northern Alabama. *J. Environ. Qual.* **2008**, *37*, 535–541.
39. Pengthamkeerati, P.; Motavalli, P. P.; Kremer, R. J.; Anderson, S. H. Soil carbon dioxide efflux from a claypan soil affected bysurface compaction and applications of poultry litter. *Agric. Ecosyst. Environ.* **2005**, *109*, 75–86.
40. Jones, S. K.; Rees, R. M.; Skiba, U. M.; Ball, B. C. Greenhouse gas emissions from a managed grassland. *Global Planet. Change* **2005**, *47*, 201–211.
41. Watts, D. B.; Way, T. R.; Torbert, H. A. Subsurface Application of Poultry Litter and its Influence on Greenhouse Gas Emissions in Permanent Pastures. *Soil Sci. Soc. Am. J.* **2011** Submitted for publication.
42. Jones, S. K.; Rees, R. M.; Kosmas, D.; Ball, B. C.; Skiba, U. M. Carbon sequestration in a temperate grassland; management and climate controls. *Soil Use Manage.* **2006**, *22*, 132–142.
43. Chadwick, D. R.; Pain, B. F.; Brookman, S. K. E. Nitrous oxide and methane emissions following application of animal manures to grassland. *J. Environ. Qual.* **2000**, *29*, 277–287.
44. Yamulki, S.; Jarvis, S. C.; Owen, P. Methane emission and uptake from soils as influenced by excreta deposition from grazing animals. *J. Environ. Qual.* **1998**, *28*, 676–682.
45. Khalil, K.; Mary, B.; Renault, P. Nitrous oxide production by nitrification and dentirfication in soil aggregates as affected by O_2 concentration. *Soil Biol. Biochem.* **2004**, *36*, 687–699.
46. Cabrera, M. L.; Chiang, S. C.; Merka, W. C.; Thompson, S. A.; Pancorbo, O. C. Nitrogen transformations in surface-applied poultry litter: effect of litter physical characteristics. *Soil Sci. Soc. Am. J.* **1993**, *57*, 1519–1525.
47. Brinson, S. E.; Cabrera, M. L.; Tyson, S. C. Ammonia volatilization from surface-applied, fresh and composted poultry litter. *Plant Soil* **1994**, *167*, 213–218.
48. Cabrera, M. L.; Chiang, S. C. Water content effect on denitrification and ammonia volatilization in poultry litter. *Soil Sci. Soc. Am. J.* **1994**, *58*, 811–816.
49. Nathan, M. V.; Malzer, G. L. Dynamics of ammonia volatilization from turkey manure and urea applied to soil. *Soil Sci. Soc. Am. J.* **1994**, *58*, 985–990.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

50. Marshall, S. B.; Wood, C. W.; Braun, L. C.; Cabrera, M. L.; Mullen, M. D.; Guertal, E. A. Ammonia volatilization from tall fescue pastures fertilized with broiler litter. *J. Environ. Qual.* **1998**, *27*, 1125–1129.
51. Sharpe, R. R.; Schomberg, H. H.; Harper, L. A.; Endale, D. M.; Jenkins, M. B.; Franzluebbers, A. J. Ammonia Volatilization from Surface-Applied Poultry Litter under Conservation Tillage Management Practices. *J. Environ. Qual.* **2004**, *33*, 1183–1188.
52. Stevens, R. J.; Logan, H. J. Determination of the volatilization of ammonia from surface applied cattle slurry by the micrometeorological mass balance method. *J. Agric. Sci.* **1987**, *109*, 205–207.
53. Whitehead, D.; Bristow, A. W. Transformations of nitrogen following the application of 15N-labelled cattle urine to an established grass sward. *J. Appl. Ecol.* **1990**, *27*, 667–678.
54. Moal, J.; Martinez, J.; Guiziou, F.; Coste, C. Ammonia volatilization following surface-applied pig and cattle slurry in France. *J. Agric. Sci.* **1995**, *125*, 245–252.
55. Colbourn, P.; Dowdell, R. Denitrification in field soils. *Plant Soil* **1984**, *76*, 213–226.
56. Lowrance, R; Johnson, J. C., Jr.; Newton, G. L.; Williams, R. G. Denitrification from soils of a year-round forage production system fertilized with liquid dairy manure. *J. Environ. Qual.* **1998**, *27*, 1504–1511.
57. Intergovernmental Panel on Climate Change. *Guidelines for National Greenhouse Gas Inventories*; Volume 4; Agriculture, Forestry and Other Land Use. Chapter 11; N_2O Emissions from Managed Soils, and CO_2 Emissions from Lime and Urea Application. 2006. URL http://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/4_Volume4/V4_11_Ch11_N2O&CO2.pdf (Accesed Feb. 22, 2011).
58. Kirchmann, H. Losses, plant uptake and utilisation of manure nitrogen during a production cycle. *Acta Agric. Scand. Suppl.* **1985**, *24*.
59. Thornton, F. C; Shurpali, N. J.; Bock, B. R.; Reddy, K. C. N_2O and NO emissions from poultry litter and urea applications to bermuda grass. *Atmos. Environ.* **1998**, *32*, 1623–1630.
60. Eichner, M. J. Nitrous oxide emissions from fertilized soils: Summary of available data. *J. Environ. Qual.* **1990**, *19*, 272–280.
61. Watts, D. B.; Torbert, H. A.; Prior, S. A. Soil Property and Landscape Position Effects on Seasonal Nitrogen Mineralization of Composted Dairy Manure. *Soil Sci.* **2010**, *175*, 27–35.
62. Marshall, S. B.; Mullen, M. D.; Cabrera, M. L.; Wood, C. W.; Braun, L. C.; Guertal, E. A. Nitrogen budget for fescue pastures fertilized with broiler litter in Major Land Resource Areas of the southeastern US. *Nutr. Cycling Agroecosyst.* **2001**, *59*, 75–83.
63. Chang, C.; Cho, C. M.; Janzen, H. H. Nitrous oxide emission from long-term manured soils. *Soil Sci. Soc. Am. J.* **1998**, *62*, 677–682.
64. Ryden, J. C. Denitrification loss from a grassland soil in the field receiving different rates of nitrogen as ammonium nitrate. *J Soil Sci.* **1983**, *34*, 355–365.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

65. Akiyama, H.; Tsuruta, H. Nitrous oxide, nitric oxide, and nitrogen dioxide fluxes from soils after manure and urea application. *J. Environ. Qual.* **2003**, *32*, 423–431.
66. Sauer, T. J.; Compston, S. R.; West, C. P.; Hernandez-Ramirez, G.; Gbur, E. E.; Parkin, T. B. Nitrous oxide emissions from a bermudagrass pasture: Interseeded winter rye and poultry litter. *Soil Biol. Biochem.* **2009**, *41*, 1417–1424.
67. Coyne, M. S.; Villalba, A.; Blevins, R. L. *Nitrous oxide loss from poultry manure-amended soil after rain. J. Environ. Qual.* **1995**, *24*, 1091–1096.
68. Coyne, M. S.; Gilfillen, R. A.; Blevins, R. L. Nitrous oxide flux from poultry-manured erosion plots and grass filters after simulated rain. *J. Environ. Qual.* **1994**, *23*, 831–834.
69. Jones, S. K.; Rees, R. M.; Sikba, U. M.; Ball, B. C. Influence of organic and mineral N fertilizer on N_2O fluxes from a temperate grassland. *Agric. Ecoyst. Environ.* **2007**, *121*, 74–83.

Downloaded by UNIV OF DELAWARE MORRIS LIB on June 20, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch025

Chapter 26

Quantification and Mitigation of Greenhouse Gas Emissions from Dairy Farms

Hamed M. El-Mashad[a,b,c] and Ruihong Zhang[*,a]

[a]Biological and Agricultural Engineering Department,
University of California, Davis
[b]Agricultural Engineering Department, Mansoura University,
El-Mansoura 35516, Egypt
[c]Current address: Agriculture and Environmental Sciences Department,
Lincoln University, Jefferson City, Missouri 65101
[*]E-mail: rhzhang@ucdavis.edu

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Agriculture activities are major emission sources of greenhouse gases (GHGs) such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). About 18% of the global anthropogenic GHGs are emitted from livestock production activities including land use. This chapter reviews the sources and quantities of GHG emissions on dairy farms. The methods commonly used for measuring and quantifying GHG emissions are presented and compared. Various mitigation strategies for reducing GHG emissions from dairy farms are discussed. These strategies include improved animal management related to animal breeding, animal housing, animal waste handling, and land application of animal manure. Potential uses of manure as a feedstock for the production of valuable products such as energy, fertilizers, chemicals and other materials are also presented. Some critical research needs are identified in the areas of mathematical modeling of GHG emissions and mitigation and in developing different technologies for manure management and utilization.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Introduction

Human activities emit many gases including greenhouse gases (GHGs) such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). The emissions of greenhouse gases lead to global warming (*1*) . The major sources of the GHGs are energy supply, transport, industry, and agriculture sectors. The emission of CO_2 increased by about 80% from 1970 to 2004, due to the vast increase in energy consumption in industrial sectors (*2*). In 2004, agricultural activities and deforestation accounted for about 31% of the global anthropogenic GHG emissions in terms of CO_2 equivalent (*2*) . Agriculture is the greatest contributor of N_2O and CH_4, accounting for about 60% and 50% of global anthropogenic emissions of the two gases, respectively (*3*) . The emissions of CH_4 and N_2O from major agricultural activities from 1990 to 2008 are shown in Figures 1 and 2. Livestock production activities, including land use, account for about 18% of the global anthropogenic GHG emissions (*4*). The main sources for the emissions of CH_4 and CO_2 from dairy cows are enteric fermentation and respiration. The stored manure is another significant source (*5*). However, animal respiration is not considered as a net source for the CO_2 emissions, because animal feed previously sequestered atmospheric CO_2 during plant growth (*4*). The emission rates of different compounds depend on animal species, feeding practices, type of confinement facility, manure management system (e.g., hadling and storage), and land application practices (*6*). The changes in the emissions over years were attributed to the dynamics of the animal population and the changes in feed quality and digestibility (*7*). The increase of CH_4 emissions over years was also attributed to the increase in liquid manure application that has higher emissions than solid manure. Agricultural soil management activities such as fertilizer application and other crop practices represented the major source of N_2O emissions. There was no significant difference in N_2O emissions during this priod of time due to the relatively constant amount of nitrogen applied to soils. In addition to the sources shown in Figures 1 and 2, CH_4 and N_2O from field burning of the agricultural resides represented respectively, about 0.5% and 0.2% of the total emissions of these compounds. Moreover, agricultural sources emit small amounts of CO_2 from the combustion of the fossil fuels to operate agricultural equipment.

The total emissions of GHGs from agricultural activities in the U.S. were estimated to be 427.5 Tg CO_2 eq in 2008, representing 6.1% of the total emissions in the U.S. (*7*). The contribution of major emission sources is shown in Figure 3. Greenhouse gases emitted from dairy farms include the net emissions of CO_2 plus the emissions of CH_4 and N_2O (*9*). Based on a life cycle analysis of milk production, CH_4 represents 50% or more of GHG emissions from milk production (*10*). Emissions of N_2O represent 27% -38% of the total emissions while CO_2 emissions represent only 5-10% of total emissions.

In this chapter, sources of GHGs (CH_4 and N_2O) in dairy farms, and quantification methods and mitigation strategies to alleviate their negative impact on the environment are discussed. According to Clemens et al. (*11*), ammonia is not considered a greenhouse gas because of its short lifetime in the atmosphere, but its deposition induces N_2O formation elsewhere.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

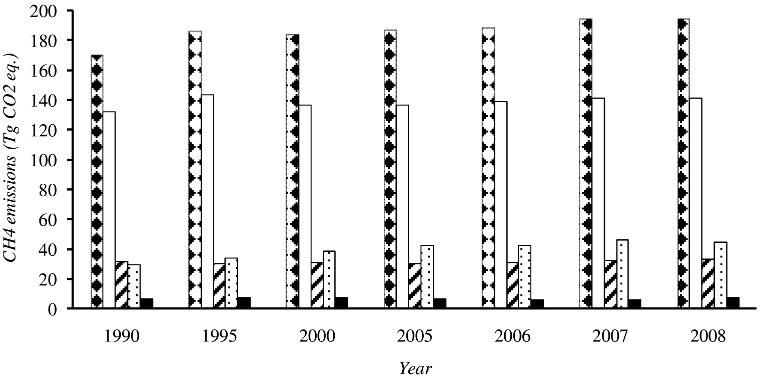


Figure 1. Total and major sources of CH_4 emissions from agricultural activities in the U.S. from 1990 to 2008 (7). These calculations were based on a global warming potential of 21 for CH_4 (8).

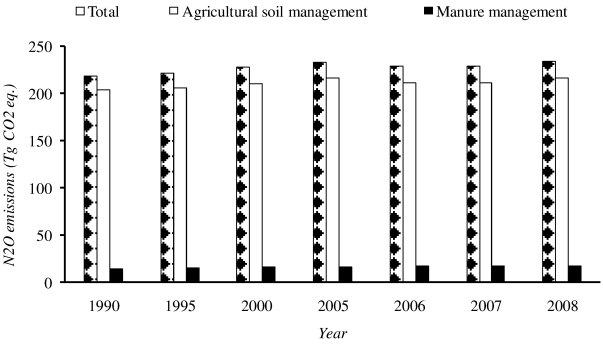


Figure 2. Total and major sources of N_2O emissions from agricultural activities in the U.S. from 1990 to 2008 (7). These calculations were based on a global warming potential of 310 for N_2O (8).

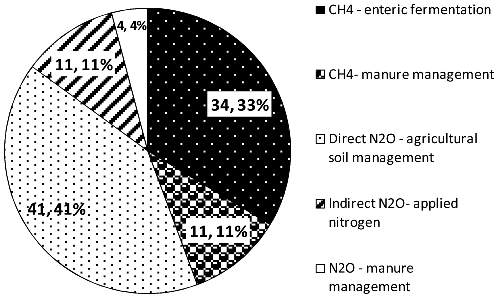


Figure 3. Emissions of CH_4 and N_2O from agricultural sector in the U.S.A. in 2008 (7).

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Sources of Greenhouse Gas Emissions on Dairy Farms

A dairy farm is a complex system consisted of some subsystems such as livestock, manure management, soil and crops (*12*). Dairy farming contributes to global warming directly through the emissions resulted from on-farm activities and indirectly through emissions from energy use, purchased goods and other N emissions (*13*). In the model developed by Rotz et al. (*9*), the emission sources of GHGs from a dariy farm were divided into primary and secondary sources (Figure 4). Primary sources include different farm activities (i.e., feed production, animal maintenance and manure handling). Secondary sources include the production of fuel, electricity, machinery, fertilizer, pesticide and other materials used in different farm activities. It can also include emissions involved in the production of replaced animals if any.

Emission Sources of Methane and Carbon Dioxide

Animals are a major source of CH_4 and CO_2 emissions on dairies. While CH_4 is produced under anaerobic conditions, CO_2 is produced and emitted from animal farms under both aerobic and anaerobic conditions as a result of the microbial decomposition of organic matter (*14*). However, the CO_2 emissions from animals and their manure do not contribute to the long term increase in atmospheric CO_2 as it is part of carbon cycle that takes place over a short time period (*6*, *14*).

Enteric fermentation is a major source of CH_4 emissions. Methane is produced by the methanogenic archaea present in rumen. Archaea are single cell microorganisms genetically different from bacteria as they have genes and metabolic pathways that are close to those of eukaryotes. About 6% –10% of the total gross energy consumed by a dairy cow is converted to CH_4 and released via the breath (*15*). This can be interpreted to an annual emission of 91-146 kg/head. The emissions of CH_4 and CO_2 were measured from a tie-stall farm housing 118 lactating cows (*16*). Emission rates of CH_4 and CO_2 were 552 and 5756 L/d per cow, respectively after subtracting the emissions from manure that were measured to be 35 and 381 L/d per cow, respectively. The factors affecting the emissions of both CH_4 and CO_2 from animals are animal type, body weight, dry matter intake; and feed digestibility (*17–20*).

In addition to enteric fermentation, emissions of CH_4 and CO_2 take place from manure collected on floors and in storages. The factors affecting the emissions of CH_4 and CO_2 from manure on floors are manure handling, frequency of manure removal, feed characteristics, weather conditions, and surface area (*9*, *21*, *22*). The factors affecting the emissions of CH_4 and CO_2 from manure storage are amount of manure, type of manure storage, weather conditions, and the presence of storage cover (*9*, *23*). Massè et al. (*24*) studied emissions of CH_4 from manure storage at 10 and 20 ^{o}C for 370 days, and concluded that frequent removal of manure in the summer would significantly reduce CH_4 emissions from manure storages.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

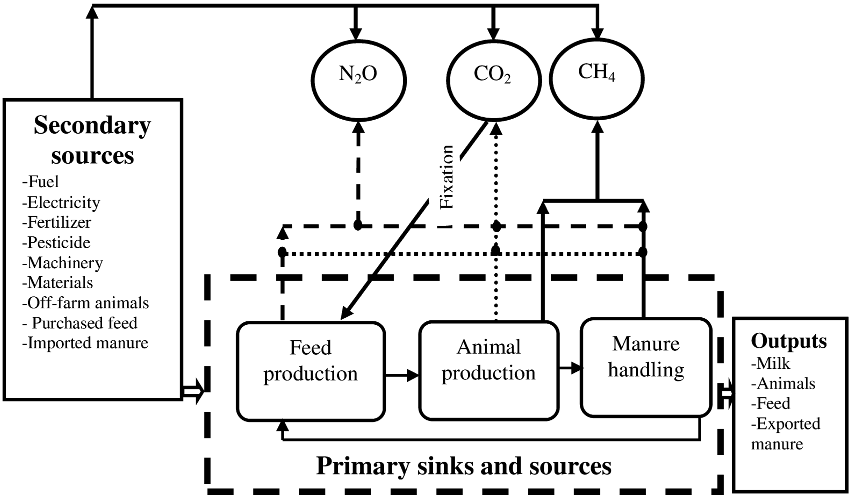

N$_2$O
CO$_2$
CH$_4$
Secondary sources
-Fuel
-Electricity
-Fertilizer
-Pesticide
-Machinery
-Materials
-Off-farm animals
- Purchased feed
-Imported manure
Fixation
Feed production
Animal production
Manure handling
Primary sinks and sources
Outputs
-Milk
-Animals
-Feed
-Exported manure

Figure 4. Sources of GHG emissions on farm (adapted from (9)).

Emission Sources of Nitrous Oxide (N_2O)

Soils are the major sites for N_2O emissions (*6*). While CH_4 and CO_2 are produced via anaerobic degradation of organic matter, N_2O is produced via nitrification and denitrification (*25*). CO_2 is also produced during the aerobic decomposition of organic matter when present in air or in soil. Among the factors affecting these two processes are degradable carbon and nitrogen, presence of oxygen, application rate of nitrogen fertilizers and soil conditions such as moisture content, ammonia content, pH, temperature, redox potential and physical properties of soils that affect gas diffusivity (*26–30*) . Soil with poor drainage has more N_2O emissions when nitrogen sources are available for nitrification and denitrification. Moreover, manure application to cropland during the growing season has less emissions of N_2O as compared with manure applied to lands in the absence of crops (*6*). This might be due to nitrogen uptake by plants. The characteristics of manure, application time and rate, soil type, and crop type are among the important factors affecting the emissions of N_2O from manure applied on grassland (*31*). Animal type is an important factor affecting the emissions of N_2O from manure due to the differences in manure compositions that resulted from the differences in diets, feed conversions and manure management (*31*).

In addition to the emissions from soils, N_2O could be emitted from crust layers formed on the surface of manure storage, stacked solid and semisolid manure, bedded pack manure on barn floors, and unpaved dry lot surfaces (*9*). The factors affecting the emissions from these sources are surface area, temperature, rainfall, characteristics of crust layer, manure characteristics (e.g., pH, C/N ratio), storage duration and manure treatment technology applied if any (e.g., (*32*)). No N_2O is formed and emitted when crust layer does not exist at the surface of liquid manure storage (*33*).

Quantification of Greenhouse Gas Emissions

Emission Factors

Quantification of the emission rate and total emissions of GHGs at the farm level is an important step before developing and implementing mitigation strategies, in order to focus on the sources of large emission sources (*3*). The most common approach used for estimating the emissions of different compounds (e.g., CH_4, NH_3, and N_2O) from animal farms is emission factors. They are derived based on the emission measurement data from a set of defined animal feed operations to obtain an average emission value, for each compound, per animal unit or per unit of production (*34*).

Table I. Emission factor of CH_4 (kg C animal^{-1} yr^{-1}) from enteric fermentation of different animals

Source	*Emission factor*	*References*
Dairy cows	76.5	(*40*)
	75.0	(*39*)
	99.7	(*41*)
	88.5	(*42*)
Heifers	47.3	(*40*)
	52.9	(*41*)
	42.0	(*42*)
Calves	36.8	(*40*)
	13.1	(*39*)
	36.8	(*41*)
	35.3	(*42*)
Young cows	46.6	(*39*)
Bulls	58.3	(*41*)
	56.3	(*42*)
Beef cows	54.0	(*42*)
Steers	35.3	(*42*)
Horses	9.8	(*42*)
Sheep	6.0	(*42*)
Goats	6.0	(*42*)

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Several methods are being applied for measuring emissions from dairy farms. Johnson and Johnson (*35*) discussed the basics, advantages and disadvantages of each method. The are two common methods for quantifying emissions from a dairy farm. The first method is to measure short term air samples taken from emission sources using enclosure techniques or tracer gas methods. The second method is to use respiration chamber sampling systems such as whole animal chambers, head boxes, or ventilated hoods and face masks. A measurement system consists mainly of sampling system, measurement device and a mean of data acquisition and storage (*36*). Near infrared sensors, including photo-acoustic and direct optical absorption sensors are commonly used for measuring the concentrations of CO_2, CH_4 and N_2O (*37*). The most common techniques for measuring CH_4 content in air are infrared spectroscopy, gas chromatography, mass spectroscopy, and tunable laser diode techniques. For direct measurements of gas concentration, measuring devices are installed on site either directly at the sampling location or at different locations. In the latter case, sample tubes and switch valves are used to transfer air sample to the measuring device (*37*). Samples could also be collected in gas tight bags and containers such as canisters and then sent off site for analysis. Tremblay and Massè (*38*) used respiration chamber approach to quantify CH_4 emissions from a herd of 21 cows over 24 h per day for a period of one year. Using pure CH_4, in the absence of animal, the accuracy of CH_4 recovery was found to be within ± 4.6% during 15 calibration tests. Hensen et al. (*39*) estimated emission factors of CH_4 and N_2O from a 1200 $m^3$of slurry storred in Wageningen, Netherlands to be 11 g CH_4 day^{-1} m^{-3} and 0.014 g N_2O day^{-1} m^{-3}, respectively. Some emission factors of CH_4 from enteric fermentation and emissions factors of CH_4 and N_2O from manure management (handling, storage, and land application) for different animals are shown in Tables I and II. As can be seen from these Tables, different emission factors were reported depending on farm and weather conditions. Dairy cows have the highest CH_4 emission factors among other animal species.

Using a single emission factor for estimating the emissions of CH_4 entails a large error in emissions calculations for farms located in a small region (*24*).This is due to the differences in farm size, dynamics of herd, farm management and manure handling systems. There are substantial uncertainties in the estimation of GHG emissions from agricultural systems in general using emission factors (*43*). They include the insufficient understanding of the system and its interactions, variability in weather conditions and the validity and the distribution of possible outcomes. Emissions are also dependent upon farm management, rations, animal age and weight (e.g., (*9*)). Therefore, process-based emission models are superior tools for estimating emission rates and total emissions by including the factors that affect emission dynamics (*34*, *44*). The U.S. Environmental Protection Agency (USEPA) recently funded a project for measuring the emissions of different gases from animal feeding operations (AFO). The study is called National Air Emissions Monitoring Study (NAEMS). It is a two-year study of emissions from different animals AFO. Eight dairies are being studied in several states. Emissions are monitored from barns and from manure lagoons. The agency anticipates finalizing the emissions estimating methodologies in June 2012. The NAMES study is expected to provide reliable data on the emission rates of different GHGs under

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

different weather conditions and farm practices. More information on the NAEMS can be found on http://www.epa.gov/airquality/agmonitoring/basicinfo.html. The results of the NAEMS could be also used to validate mathematical models for the estimation of GHG emissions.

Modeling of Greenhouse Gas Emissions

The GHG emission models are used for selecting cost-effective mitigation strategies. They can also be used in extension and teaching (*45*). There are two approaches that can be used for modeling the emissions of GHGs on animal farms. The first is empirical and the other is mechanistic approach. Both types of models allow the calculation of emissions of different GHGs as a function of certain input variables. The empirical models are derived based on experimental data that are collected under different conditions. In this approach, regression equations are derived to correlate the emissions of different GHGs with some of the factors affecting the emissions. These models are generally black box models where the processes (physical, biochemical, and mass transfer) that control the emissions are not distinguished rather the effects of these processes are lumped in certain variables that drive the emissions. Empirical models are limited to the range of experimental conditions used to derive the models and do not allow the possibility of changing certain input variables that influence specific processes that involved in generation source, and transportation of GHGs from the source to the atmospher.

On the other hand, the mechanistic approach depends on understanding different processes (physical, biochemical, and mass transfer) that govern the generation and transportation of different GHGs. Mechanistic models are usually derived using mathermatical equations including differential equations and laws of physics, chemistry and mass transfer. However, in some instants (e.g., absence of understanding of a certain process), mechanistic models can include some empirical models. Mechanistic models for simulating GHG emissions from dairy farms are usually divided into submodels. These submodels may include submodels for emissions from animals, housing, manure storage and land applications (Figure 5). Many input parameters can be included in mechanistic models so that it would be possible to accurately predict the emissions of different GHGs. Mechanistic models in some cases are superior over empirical models. This is because validated mechanistic models can be applied to predict the emissions under a wide range of variables that affect the emissions of GHGs. Users of validated mechanistic models can analyze the influence of different weather conditions, farm designes, farm management, manure handling and manure application systems. With using detailed and validated mechanistic models, it could be possible to develop cost effective and practical mitigation strategies for GHGs on the whole farm or for the sources that cause major emissions. Kebreab et al. (*46*) concluded that mechanistic models are more accurate when estimating the national emissions of CH_4 from enteric fermentation. This is due to the fact that these models are based on the mathematical representation of biochemical processes involved in ruminal fermentation. Moreover the chacteristics of animal diet is an important input parameter for these models. The main drawback of mechanic models is that they are more complex, contain more mathematical questions contain more input parameters, and require more time and mathematical and modeling skills to develop as compared to empirical models.

Table II. Emission factors of CH_4 (kg C animal^{-1} yr^{-1}) and N_2O (kg N animal^{-1} yr^{-1}) from manure management

Type of animal	*CH_4 emission factor*	*N_2O emission factor*	*References*
Dairy cow	7.1	114.7	(*41*)
	27.0	--	(*42*)
Bulls	3.4	57.6	(*41*)
	0.8	--	(*42*)
Beef cow	0.8	--	(*42*)
Suckler cow	2.0	33.6	(*41*)
Heifer	2.2	39.8	(*41*)
	27.0	--	(*42*)
Beef heifer	0.8	--	(*42*)
Calve	1.4	26.2	(*41*)
	0.8	---	(*42*)
Steers	0.8	---	(*42*)
Horses	1.1	---	(*42*)
Sheep	0.1	---	(*42*)
Goats	0.1	---	(*42*)

Models are usually used for quantifying CH_4 emissions from enteric fermentation (*46*). Models based on fermentation balance or feed characteristics have been used to estimate CH_4 production from animals (*35*). Mechanistic (*e.g.,* (*47*)) and empirical models (e.g., (*48*)) were used for calculating CH_4 emissions from enteric fermentation. Sommer et al. (*20*) developed a mathematical model for prediction of CH_4 and N_2O emissions during handling and use of liquid manure. Their results showed that N_2O and CH_4 emissions from cattle slurry could be reduced by 71% if slurry is anaerobically digested. A whole farm model called DairyWise was developed by Schils et al. (*12*), which can be used to predict the changes in farm management. The model can accurately predict the flow of materials and nutrients inside a farm. It can also predict the exchange of these resources between the farming system and the surroundings. The model has a submodel for estimating the GHG emissions from dairy farms using emission factors from Dutch emission inventories. The emission from enteric fermentation was calculated based on an emission factor per each dry matter uptake. Emission from manure was separately calculated from stored manure and from manure excreted during grazing.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

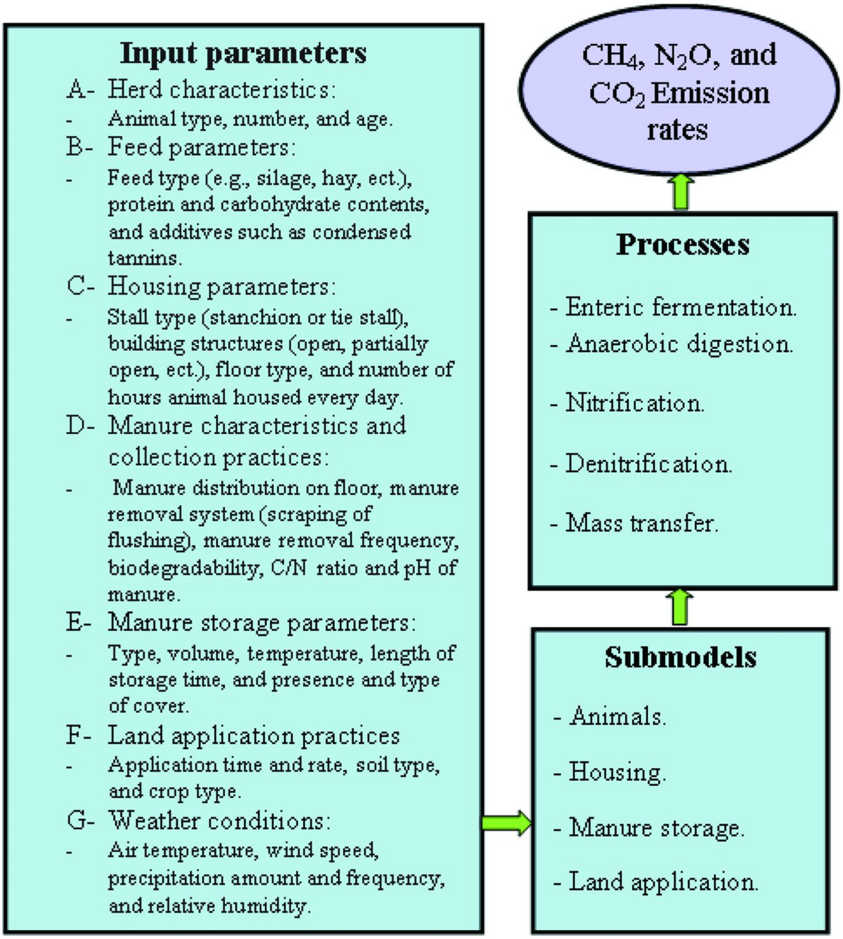

Input parameters
A- Herd characteristics:
- Animal type, number, and age.
B- Feed parameters:
- Feed type (e.g., silage, hay, ect.), protein and carbohydrate contents, and additives such as condensed tannins.
C- Housing parameters:
- Stall type (stanchion or tie stall), building structures (open, partially open, ect.), floor type, and number of hours animal housed every day.
D- Manure characteristics and collection practices:
- Manure distribution on floor, manure removal system (scraping of flushing), manure removal frequency, biodegradability, C/N ratio and pH of manure.
E- Manure storage parameters:
- Type, volume, temperature, length of storage time, and presence and type of cover.
F- Land application practices
- Application time and rate, soil type, and crop type.
G- Weather conditions:
- Air temperature, wind speed, precipitation amount and frequency, and relative humidity.
CH_4, N_2O, and CO_2 Emission rates
Processes
- Enteric fermentation.
- Anaerobic digestion.
- Nitrification.
- Denitrification.
- Mass transfer.
Submodels
- Animals.
- Housing.
- Manure storage.
- Land application.

Figure 5. Important input parameters and processes involved in mechanistic models.

Strategies for Mitigating the Greenhouse Gas Emissions

Emissions reductions of gaseous compounds from animal farms could be achieved using different approaches such as nutritional management, modification of design of animal housing and manure storage, end-of-pipe air treatment, and animal manure treatment and management (*49*). Three scenarios were reviewed for the reduction of GHG emissions by Casey and Holden (*50*): improve milk production from cows so that fewer animals could supply the national milk quota,

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

slaughter as many non-milk producing animals (i.e., slaughter scheme), and combination of use of efficient cows with extensive management and elimination of non-milking animals. The third scenario achieved the lowest GHG emissions. Emissions from enteric fermentation could be reduced by 28-33%. While the first and second scenarios could reduce the emissions by about 14-18% and 14-26%, respectively.

Weiske et al. (*51*) discussed different measures for GHG mitigations in dairy farms: optimizing lifetime efficiency of dairy cows, frequent removal of manure, anaerobic digestion of manure, and improved manure application techniques. Anaerobic digestion with capturing the produced biogas was considered as one of the effective mitigation measures for methane and and nitrous oxide emissions. This approach can eliminate CH_4 emissions by converting it to energy source and therefore reduce the fossil fuel consumption on farm. It can also prevent N_2O formation by restricting oxygen, a precursor for nitrification of NH_4^+ to N_2O.

The control of the emission of a certain compound from manure might enhance the emission of another compound or even of the same compounds at another state of management (*32*) . For example, although anaerobic digestion reduces CH_4 emissions, the low total solids of the digestate facilitate its infiltration into the soil, which reduced NH_3 emission after application. However, the increased pH and NH^+_4 content during digestion increases the potential of NH_3 emissions.

Mitigation of Methane Emissions

Mitigation of Emissions from Enteric Fermentation

Mitigation strategies for CH_4 emissions from enteric fermentation were reviewed and are shown in Table III (*15*). The choice of a mitigation strategy depends on farm size, farm location, availability of resources and economic issues. Improving feed conversion efficiency and reducing the number of animal could reduce CH_4 emissions from the enteric fermentation (*41*). Increasing grain and soluble carbohydrates in animal ration decreases CH_4 emissions as a result of decreasing acetate concentrations (*52*). This is due to the fact that acetate is a main intermediate product for methane production.

Mitigation of Methane Emissions from Manure Storage

Controlled anaerobic digestion of manure can reduce GHG emissions directly by the reduction in CO_2 equivalent emissions and CO_2 saving by biogas energy that displaces fossil fuels and indirectly by reducing the nitrogen fertilizer production and use (*41*). Moreover, digested slurry emitted less GHGs during storage than untreated slurry (*11*). Anaerobic digestion could reduce up to 90% of CH_4 emissions from manure storage (*20*).

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Table III. Strategies for mitigating enteric CH_4 emission (*15*)

Categories of mitigation strategies	*Subcategories of mitigation strategies*	*Measures*
Animal manipulation	Animal breeding	- Improving feed conversion efficiency with using low feed intake, - Breeding ruminants with lower CH_4 production.
	Animal management system	- Reducing the number of unproductive animals on a farm, - Extended lactation in dairying, - Applying novel production systems.
Diet manipulation	Forage quality	- Feeding forages with low fiber and higher soluble carbohydrates, - Changing from C_4 to C_3 grasses, - Addition of grain to forage diet increases starch and reduces fiber intake, - Grazing on less mature pastures.
	Plant breeding and plants secondary compounds	- Increasing lipids and condensed tannins in forages, - Improve the digestability of feeds. - Increasing plant saponins and condensed tannins concentration in diets.
	Dietary supplements	- Addition of yeasts, dietary oils, enzymes, dicarboxylic acids (e.g., fumarate, malate, and acrylate).
Rumen manipulation	Biological control strategies	- Inhibition of methanogenesis (e.g., using bacteriophages), - Redirecting H_2 to propionate producers or acetogens, - Using bromochloromethane, chloroform and monesin as inhibitors for CH_4 formation.
	Vaccination	- Development of vaccines to control methanogens.

Covering manure during storage and applying solid-liquid separation were also found to be effective methods for mitigation of GHG emissions. Chadwick (*53*) studied the effect of compaction and covering during storage of farm yard manure on the emission of NH_3, CH_4 and N_2O. The results showed that compaction and covering significantly reduced emissions of NH_3 and N_2O. No significant differences were found on emissions of CH_4 from digested slurry in storages with or without a straw cover (*11*). However, using wooden cover reduced the emission

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

significantly. The effect of mixing manure with straw on GHG emissions was studied by Yamulki (*54*). Results showed that adding straw could be a promising strategy for reducing GHG emissions. The author attributed the reduction to the lowered mineralization at high C/N ratio and the increased aeration at the lower moisture content that resulted from the addition of straw.

Amon et al. (*32*) studied the effects of solid-liquid separation with composting of solid fraction, anaerobic digestion, slurry aeration and straw cover on emissions of CH_4, NH_3 and N_2O from liquid manure storages for 80 days and after manure application under field conditions. Ammonia emission after land application of the liquid fraction of mechanically separated manure was lower than that of untreated manure. However, a large amount of ammonia was emitted during composting of the solid fraction. CH_4 emissions after land application were small with all treatments as compared with the emission during storage. Mechanical separation of solid fraction decreases the CH_4 emissions by about 42%. During storage the lowest CH_4 emissions were measured from the anaerobically digested manure due to the fact that most of the biodegradable organics were consumed during digestion process. The amount of manure remaining for land application after emptying the storage had a considerable effect on CH_4 emissions as it can be a source of adapted inoculum for CH_4 production (*24*). Therefore, frequent cleaning of manure storage could be a strategy for reducing the emissions of CH_4. Cleaning manure storage assures the reduction of the amount of remaining manure that could carry enough inoculum for the new manure added to storage.

Mitigation of Nitrous Oxide Emissions

Many strategies are being applied for mitigation of the emissions of N_2O. The selection of a mitigation strategy depends on farm size and farm practice (e.g., type of manure storage and manure handling and processing). Managed grasslands are the main source of N_2O emission in dairy farming systems (*55*). Mitigation of N_2O emission from these grasslands could be achieved by improved nitrogen fertilizer management, improved grassland management and improved management of livestock production. Improve nitrogen management (e.g., reduction of ammonia volatilization and use corn silage) could achieve up to 70% reduction of N_2O emissions from dairy farming systems. Corn silage has low concentrations of total protein, and therefore low amounts of nitrogen could be excreted when animal is fed corn silage (*56*). Application of nitrification inhibitor (e.g., dicyandiamide) in grazed pasture soil significantly decreased N_2O emissions from animal urine patches by 56–73% (*57*). The nitrification inhibitor slows down the rate of the conversion of NH_4^+ to NO_2 and NO_3, and thus to N_2O (*58*). Therefore, nitrification inhibitors reduce N_2O emissions from nitrification and denitrification processes (*59*).

Table IV summarizes potential mitigation measures for N_2O emissions (*15*). Some of the measures are based on improving nitrogen recycling in animal systems and producing genetic modified animals. Such measures include increasing the frequency and distributed area of urine either with feed or genetic manipulations; decreasing the concentration of nitrogen in urine and increasing urination frequency by addition of salts that increase the water intake; and feed additions such as condensed tannins that protect the degradation of proteins in animals. Other measures are based on reducing emissions from soils such as controlling the rate and timing of applications of animal manures and nitrogen fertilizers; injecting and incorporation of animal manure in soils; application of nitrification inhibitors; irrigation and drainage management; and grazing on wet soils. Emissions of N_2O could also be reduced by breeding plants that use nitrogen more efficiently, thus producing high energy to protein ratios. Aerated and straw covered manure had the highest N_2O emission during storage (*32*). After land application, digested slurry had the lowest emissions of N_2O as compared with other treatments due to the low dry matter contents. Using impermeable covers for manure storage could inhibit N_2O emissions by depriving oxygen inside the storage (*11*). Lower emissions of CH_4 and N_2O were found when applying dairy slurry to dry soils as compared with wet soils (*31*). Lower emission of N_2O was also measured during summer than during spring due to the greater plant uptake and increased ammonia volatilization in warming weather conditions.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Table IV. Strategies for mitigation of N_2O emission (*15*)

Categories of mitigation strategies	*Subcategories of mitigation strategies*	*Measures*
Soils	Fertilizers and manure applications	- Controlling the source, rate and timing of application of manure and N fertilizer, - Selection of application technique (e.g., injection of manure could increase the direct emissions of N_2O but can decrease the indirect emissions of N_2O due to the reduction of ammonia volatilization), - Adjusting the moisture content of soils before application, - Application of N fertilizer at least three days after manure application. -
	Nitrification inhibitors	- Applying nitrification-inhibitors-coated fertilizers and spray nitrification inhibitors such as nitrapyrin and dicyandiamide, - Feeding inhibitor to animals, - Breeding plants that secrete natural nitrification inhibitors from their roots.

Continued on next page.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Table IV. (Continued). Strategies for mitigation of N_2O emission (*15*)

Categories of mitigation strategies	*Subcategories of mitigation strategies*	*Measures*
	Grazing management	- Restricting grazing on wet soils, - Reducing grazing time and N-fertilizer application rates.
	Irrigation and drainage	- Irrigation through dry seasons, - Reducing water logging of pastures, - Well drained soils is denitrified less efficiently than waterlogged soils.
Animals	Animal breeding	- Genetic modification to improve the N conversion efficiency within the rumen, - Produce animal with more frequent urination that leads to less N concentration in urine, - Produce animal that walk while urination that leads to greater urine spread.
	Animal diet	- Balancing the protein-energy ratios, - Using high sugar varieties of ryegrass, - Addition of condensed tannins extracts, - Salt supplementation increases water intake and thus reducing the urinary N concentration and increases the urination events.
Plants	Plant breeding	- Forages that use N more efficiently, - Forages that have a higher energy-to-protein ratio, - Producing forages with high tannin contents.

Alternative Uses of Animal Manure To Mitigate Greenhouse Gas Emissions

Effective development and implementation of new technologies for alternative uses of animal manure are expected to result in significant reduction of GHG emissions from manure sources. Different products can be produced from manure (Figure 6). Alternative uses of animal manure can be in three categories: (1) conversion and use as an energy source, and (2) conversion to value-added products and (3) innovative and emerging products (*60*).

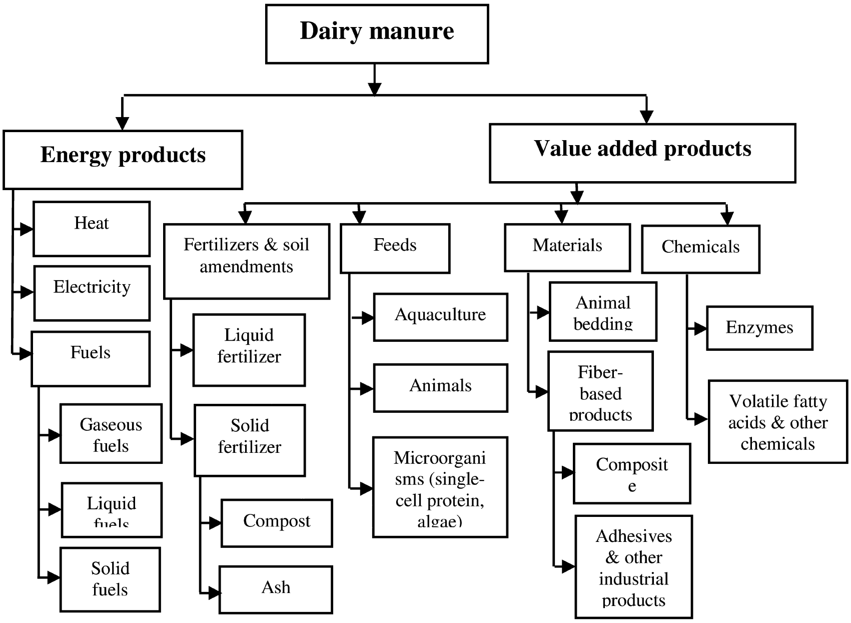

Dairy manure
Energy products
Value added products
Heat
Electricity
Fuels
Gaseous fuels
Liquid fuels
Solid fuels
Fertilizers & soil amendments
Liquid fertilizer
Solid fertilizer
Compost
Ash
Feeds
Aquaculture
Animals
Microorganisms (single-cell protein, algae)
Materials
Animal bedding
Fiber-based products
Composite
Adhesives & other industrial products
Chemicals
Enzymes
Volatile fatty acids & other chemicals

Figure 6. Alternative uses of dairy manure for energy and value-added products.

Many technologies and strategies already exist for converting animal manure into energy and other valuable products and new technologies are also being developed with better efficiencies and/or new products. The current status of various manure treatment technologies are reviewed in various literature, including reports produced by USEPA (*60*) and San Joaquin Valley Dairy Manure Technology Feasibility Assessment Panel (*61*). Research and development are needed to apply these technologies to the processing of dairy manure and develop stable and high quality products to meet consumer demand. In order to successfully produce and market the products derived from dairy manure, concerted effort is needed on several fronts, including technology development and demonstration, market development and testing, and policies. The overall environmental impact of alternative uses needs to be assessed when pursuing the maximum economic benefits.

Odor and pathogen free are the basic requirements for manure derived products. Various technologies need to be applied to transform the manure or its constituents into desirable products. Emissions and effluent management for these manure processing facilities must be carefully controlled to minimize the environmental and public health impact. Energy products that can be derived from dairy manure include heat and biofuels, which include gaseous, liquid or solid fuels. Gaseous fuels include syngas produced from thermal gasification and biogas from anaerobic digestion. Liquid fuels include alcohols produced from fermentation and thermal oil from pyrolysis or hydrothermal liquification. Solid fuels are densified products such as pellets made from fibers. Based on the facts that animal manure has complex chemical compositions and high moisture content, biogas production via anaerobic digestion processes appears to be the

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

most energy efficient choice. Biogas is typically 50-70 % CH_4 with the rest mainly being CO_2 and small quantities of moisture and other compounds. By removing moisture, CO_2 and impurities, biogas can be upgraded to biomethane, a product equivalent to natural gas. The biomethane can be supplied to the existing and future natural gas distribution systems. For dairy manure to become effective feedstock for thermal processes, such as combustion and gasification, the manure needs to be dried to lower the moisture content to less than 50%. Manure collected from corals and solids separated from freestall manure could be more suitable. Alcohol production from the fibers separated from dairy manure could have good potential as they contain up to 70% cellulose and hemicelluloses. As the technologies for producing alcohols from lignocellulosic materials become more efficient and cost competitive, manure fibers may have increased values as feedstock supply for alcohol production. Manufacturing solid fuel such as pellets and briquettes from manure fibers for biomass power plants could see increased interest in the future.

The value added products include fertilizer, feed, chemicals and biobased industrial products. Manufacturing high quality fertilizer products from raw manure or the effluent of other manure processing operations (e.g. anaerobic digesters) requires specially designed technologies to meet the nutrient and product specification of fertilizer industry. Up to 50% of nitrogen and other nutrient elements are tied up in organic compounds in the manure as excreted. Manure treatment is normally needed to transform these elements into inorganic forms so that they become readily available when they are provided to the plants. Composted dairy manure has been well recognized as an excellent soil amendment and fertilizer. It can be also used as bedding materials for animals or growth media for mushroom. The nutrients contained in the liquid streams are more challenging to manage as they are mixed with salt elements. Developing new technologies to separate nutrients from salts is necessary in order to develop high value fertilizer products. Using dairy manure as feed additives is practiced in some countries. Pathogens transfer, health risk, public relations, and nutrient digestibility are concerns that will need to be addressed. Dairy manure is an excellent nutrient source for growing various microorganisms for production of enzymes, various chemicals (e.g. volatile fatty acids), and microbial products (e.g. single-cell protein and algae). This is relatively a new research area. The most abundant components in the dairy manure are fibers. These fibers are now called animal-processed fibers (APF) (*62*). The fibers separated from raw manure or the effluent of other processes, such as anaerobic digesters, could be used in animal bedding and potting soil or could be potentially become a valuable supplement in the paper, pulp, and wood industries for manufacturing fiber-derived composite products (e.g. fiberboard, particleboard, floor tiling, and siding) and as a binding agent in adhesives, industrial tape and masonry patching materials (*62*).

In the past, most of the research and development effort has been focused on energy production and fertilizer applications of dairy manure. As regulatory and market based incentives for production of bioenergy and biobased products become stronger driving forces, new opportunities have emerged and continue to expand for dairy and other biobased industries to invest in the development and deployment of various biorefinery technologies and business strategies for

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

creating multiple revenues from dairy manure so that dairy manure could truly become a valuable resource, rather than a waste for disposal. This will require the dairy industry to re-evaluate current manure handling and management systems, make necessary changes in the manure collection methods and develop and implement new processing technologies in order to meet the consumer requirements for supplying dairy manure either as a biomass feedstock or products.

Summary and Conclusions

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Greenhouse gas emissions from dairy farms are considered to be one of the major air quality problems facing the dairy industries. The main sources of GHG emissions on farms are enteric fermentation and manure during storage and after application to lands. Effective mitigation strategies are needed to alleviate the negative effects of these gases on the environment. Quantification of the amount of GHG emissions is the first step towards developing cost effective mitigation strategies. The most common methodology for estimating GHG emissions from dairy farms is to use emission factors. This approach is seriously limited because emission factors do not normally account for the dynamics of GHG emissions associated with the changes of both farm management and weather conditions. Some mechanistic models have been developed to estimate GHG emissions under different farm management and weather conditions. However, validation of these models is still lacking. More research is needed for further development of these models to calculate emissions from different sources, animal feeding and manure management practices and under different weather conditions. Many strategies were identified in the literature for mitigation of CH_4 and N_2O emissions. These include genetic improvement of animals to increase feed conversion efficiencies of animals, producing high quality feeds with high energy to proteins ratios, dietary supplements, manure treatment technologies, and manure and soil additives. The mitigation potential and effectiveness of these proposed mitigation measures should be evaluated under various management scenarios. Mathematical models can play a substantial role in this regard. The following research needs can be identified for further development of science and technologies for creating and realizing the values from animal manure:

1. Identifying and developing markets for dairy manure derived products and understanding the requirements for manure properties and characteristics in order to supply the manure as a valuable biomass feedstock.
2. Developing literature, publications and educational programs to market dairy manure effectively as designer products.
3. Developing innovative manure collection and processing methods for meeting the requirements of different consumer requirements for dairy manure or manure derived products.
4. Conducting both basic and applied research and demonstrating commercial scale manure conversion and biorefinery technologies:

- Pretreatment processes to make the manure solids more biologically degradable;
- Advanced high-rate anaerobic processes for biomethane production and integrated waste management;
- Lignocellulosic fermentation for alcohol production;
- Solid fuel production and structural material manufacturing from manure solids;
- Thermochemical biomass-to-liquids (BTL) processes for making renewable diesels, gasolines, alcohols, and other fungible products;
- Advanced integrated biochemical and thermochemical biorefineries for improved yields and reduced cost;
- Advanced separation techniques for nutrient-salt separation;
- Advanced separation techniques for fiber and other component separation;
- High quality solid and liquid fertilizer products; and
- High quality growth media products for plants and microorganisms.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

References

1. United Nations Framework Convention on Climate Change (UNFCCC). *Kyoto Protocol to the United Nations Framework Convention on Climate Change*; FCCC/CP/L7/Add.1, 10 December 1997; UN, New York, NY.
2. Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2007: Synthesis Report*, Core Writing Team, Pachauri, R. K., Reisinger, A., Eds.; Geneva, Switzerland, 2007; p 104.
3. Intergovernmental Panel on Climate Change (IPCC). *IPCC Fourth Assessment Report: Climate Change 2007: Mitigation of Climate Change*. Metz, B., Davidson, O. R., Bosch, P. R., Dave, R., Meyer, L. A., Eds.; Cambridge University Press: Cambridge, United Kingdom and New York, 2007.
4. Steinfeld, H.; Gerber, P.; Wassenaar, T.; Castel, V.; Rosales, M.; Haan, C. de. *Livestock's Long Shadow; Environmental issues and Options*; 2006; URL http://www.fao.org/docrep.010/a0701e/a0701e00.htm.
5. Hamilton, S. W.; DePeters, E. J.; McGarvey, J. A.; Lathrop, J.; Mitloehner, F. M. *J. Environ. Qual.* **2010**, *39*, 106–114.
6. Spellman, F. R.; Whiting, N. E. *Environmental Management of Concentrated Animal Feeding Operations*; CRC Press, Taylor & Francis Group: New York, 2007**.**
7. Unitd States Environmental Protection Agency (USEPA). *Inventory of US Greenhouse Gas emissions and Sinks: 1990 – 2008*; URL http://www.epa.gov/climatechange/emissions/downloads10/US-GHG-Inventory-2010_Report.pdf.
8. Intergovernmental Panel on Climate Change (IPCC). *Greenhouse Gas Inventory Reference Manual; Revised 1996 IPCC Guidelines for National*

Greenhouse Gas Inventories, Vol. 3 (Paris, France, 1997); URL http://www.ipcc-nggip.iges.or.jp/public/gl/invs6.html.

9. Rotz, A. C.; Montes, F.; Chianese, D. S. *J. Dairy Sci.* **2010**, *93*, 1266–1282.
10. Food and Agriculture Organization (FAO). *Greenhouse Gas Emissions from the Dairy Sector a Life Cycle Assessment*; 2010; URL http://www.fao.org/docrep/012/k7930e/k7930e00.pdf .
11. Clemens, J.; Trimborn, M.; Weiland, P.; Amon, B. *Agric., Ecosys. Environ.* **2006**, *112*, 171–177.
12. Schils, R. L. M.; de Haan, M. H. A.; Hemmer, J. G. A.; van den Pol-van Dasselaar, A.; de Boer, J. A.; Evers, A. G.; Holshof, G.; van Middelkoop, J. C.; Zom, R. L. G. *J. Dairy Sci.* **2007**, *90*, 5334–5346.
13. Schils, R. L. M.; Verhagen, A.; Aarts, H. F. M.; Kuikman, P. J.; Šebek, L. B. *J. Global Change Biol.* **2006**, *12*, 382–391.
14. Unitd States Environmental Protection Agency (USEPA). *Emissions From Animal Feeding Operations*; EPA Contract No. 68-D6-0011; 2001; URL www.epa.gov/ttnchie1/ap42/ch09/draft/draftanimalfeed.pdf.
15. Eckard, R. J.; Grainger, C.; de Klein, C. A. M. *Livestock Sci.* **2010**, *130*, 47–56.
16. Kinsman, R.; Sauer, F. D.; Jackson, H. A.; Wolynetz, M. S. *J. Dairy Sci.* **1995**, *78*, 2760–2766.
17. Chianese, D. S.; Rotz, C. A.; Richard, T. L. *Trans. ASABE* **2009**, *52*, 1313–1323.
18. Wilkerson, V. A.; Casper, D. P.; Mertens, D. R. *J. Dairy Sci.* **1995**, *78*, 2402–2414.
19. Monteny, G. J.; Groenestein, C. M.; Hilhorst, M. A. *Nutr. Cycl. Agroecosyst.* **2001**, *60*, 123–132.
20. Sommer, S. G.; Petersen, S. O.; Møller, H. B. *Nutr. Cycl. Agroecosyst.* **2004**, *69*, 143–154.
21. Sommer, S. G.; Sherlock, R. R.; Khan, R. Z. *Soil Biol. Biochem.* **1996**, *28*, 1541–1544.
22. Sherlock, R. R.; Sommer, S. G.; Khan, R. Z.; Wood, C. W.; Guertal, E. A.; Freney, J. R.; Dawson, C. O.; Cameron, K. C. *J. Environ. Qual.* **2002**, *31*, 1491–1501.
23. Chadwick, D. R.; Sneath, R. W.; Phillips, V. R.; Pain, B. F. *Atmos. Environ.* **1999**, *33*, 3345–3354.
24. Massè, D. I.; Masse, L.; Claveau, S.; Benchaar, C.; Thomas, O. *Trans ASABE* **2008**, *51*, 1775–1781.
25. Monteny, G. J.; Bannink, A.; Chadwick, D. *Agric., Ecosys. Environ.* **2006**, *112*, 163–170.
26. Eichner, M. J. *J. Environ.Qual.* **1990**, *19*, 272–280.
27. Maag, M. *Mitt. Dtsch. Boden. Ges.* **1990**, *60*, 205–210.
28. Parton, W. J.; Holland, E. A.; Del Grosso, S. J.; Hartman, M. D.; Martin, R. E.; Mosier, A. R.; Ojima, D. S.; Schimel, D. S. *J. Geophys. Res.* **2001**, *106* (D15), 17403–17419.
29. Parton, W. J.; Mosier, A. R.; Ojima, D. S.; Valentine, D. W.; Schimel, D. S.; Weier, K.; Kulmala, K. E. *Global Biogeochem. Cycles* **1996**, *10*, 401–412.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

30. Johnson, J. M. F.; Franzluebbers, A. J.; Weyers, S. L.; Reicosky, D. C. *Environ. Pollut.* **2007**, *150*, 107–124.
31. Chadwick, D. R.; Pain, B. F.; Brookman, S. K. E. *J. Environ. Qual.* **2000**, *29*, 277–287.
32. Amon, B.; Kryvoruchko, V.; Amon, T. ; Zechmeister-Boltenstern, S. (2006). *Agric., Ecosys. Environ.* 2006, 112, 153-162.
33. Chianese, D. S.; Rotz, C. A.; Richard, T. L. *Appl. Eng. Agric.* **2009**, *25*, 431–442.
34. National Research Council (NRC). *Air Emissions from Animal Feeding Operations: Current Knowledge, Future Needs*; The National Academies Press: Washington, DC, 2003
35. Johnson, K. A.; Johnson, D. E. *J. Animal Sci.* **1995**, *73*, 2483–2492.
36. Saha, S.; Islam, M. T.; Hossain, M. Z. *J. Eng. Appl. Sci.* **2006**, *1*, 26–32.
37. Teye, F. K. Ph.D. dissertation, Faculty of Agriculture and Forestry, University of Helsinki, Finland, 2008**.**
38. Tremblay, F. J. B.; Massè, D. I. *Can. Biosys. Eng.* **2008**, *50*, 721–728.
39. Hensen, A.; Groot, T. T.; van den Bulk, W. C. M.; Vermeulen, A. T.; Olesen, J. E.; Schelde, K. *Agric., Ecosyst. Environ.* **2006**, *112*, 146–152.
40. Van Amstel, A. R.; Swart, R. J.; Krol, M. S. *Methane, the Other Greenhouse Gas. Research and Policy in the Netherlands*; RijksInstituut voor Volksgezondheid en Milieu: Bilthoven, 1993.
41. Kaparaju, P.; Rintala, J. *Renew. Energ.* **2011**, *36*, 31–41.
42. Division Environment Canada; URL http://www.ec.gc.ca/pdb/ghg/1990_00_report/acknow_e.cf.
43. Gibbons, M.; Ramsden, S. J.; Blake, A. *Agric., Ecosyst. Environ.* **2006**, *112*, 347–355.
44. Zhang, R.; Mitloehner, F.; Rumsey, T.; El-Mashad, H. M. ; Li, C.; Salas, W.; Rotz, A.; Hafner, S.; Montes, F.; Arogo, J.; Xin, H.; Ni., J. *Process Based Emission Models for Predicting Gaseous Emissions from Animal Feeding Operations*; White paper for Agricultural Air Quality Task Force, 2009**.**
45. Schils, R. L. M.; Olesen, J. E.; del Prado, A.; Soussana, J. F. *Livestock Sci.* **2007**, *112*, 240–251.
46. Kebreab, E.; Johnson, K. A.; Archibeque, S. L.; Pape, D.; Wirth, T. *J. Animal Sci.* **2008**, *86*, 2738–2748.
47. Baldwin, R. L. *Modeling Ruminant Digestion and Metabolism;* Chapman & Hall: London, U.K., 1995.
48. Intergovernmental Panel on Climate Change (IPCC). *2006 IPCC Guidelines for National Greenhouse Gas Inventories*; IGES, Hayama, Kanagawa, Japan; URL http://www.ipcc-nggip.iges.or.jp.
49. Melse, R. W. Ph.D. dessertation, Wageningen University, The Netherlands, 2009.
50. Casey, J. W.; Holden, N. M. *Agric. Syst.* **2005**, *86*, 97–114.
51. Weiske, A.; Vabitsch, A.; Olesen, J. E.; Schelde, K.; Michel, J.; Friedrich, R.; Kaltschmitt, M. *Agric., Ecosys. Environ.* **2006**, *112*, 221–232.
52. Chase, L. E. *Methane emissions from dairy cattle.* In the Proceedings of Mitigating Air Emissions from Animal Feeding Operations Conference, IA, May 2008**.**

53. Chadwick, D. R. *Atmos. Environ.* **2004**, *39* (4), 787–799.
54. Yamulki, S. *Agric., Ecosys. Environ.* **2006**, *112*, 140–145.
55. Velthof, G. L.; van Beusichem, M. L.; Oenema, O. *Environ. Poll.* **1998**, *102*, 173–178.
56. Rotz, C. A. *J. Anim. Sci.* **2004**, *82* (E. Suppl.), E119–E137.
57. Di, H. J.; Cameron, K. C. *Biol. Fert. Soils* **2006**, *42*, 472–480.
58. Amberger, A. *Commun Soil Sci. Plant Anal.* **1989**, *20*, 1933–1955.
59. Di, H. J.; Cameron, K. C. *Aust. J. Soil Res.* **2008**, *46*, 76–82.
60. Unitd States Environmental Protection Agency (USEPA). *Alternative Technologies Uses of Manure*; URL http://www.epa.gov/npdes/pubs/cafo_report.pdf.
61. San Joaquin Valley Dairy Manure Technology Feasibility Assessment Panel; URL www.arb.ca.gov/ag/caf/dairypnl/dairypnl.htm.
62. Sims, B. *Biomass Mag.* **2007**, *11*, 36–41.

Downloaded by PENNSYLVANIA STATE UNIV on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ch026

Downloaded by STANFORD UNIV GREEN LIBR on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ot001

Editors' Biographies

Lei Guo

Dr. Lei Guo is an Air Pollution Specialist with the California Air Resource Board (CARB). Dr. Guo has been working in environmental research and consulting for more than 20 years, and has published extensively in the field of environmental chemistry and modeling. She is the lead scientist at CARB on agricultural greenhouse gas issues, and serves as the key technical staff on the nitrous oxide working group that oversees the California research program on nitrous oxide emissions, funded jointly by multiple state agencies. Dr. Guo obtained her B.S. in Agronomy and M.S. in Environmental Sciences from Zhejiang University, Hangzhou, Zhejiang, China, and her Ph.D. in Soil Science from the University of Illinois at Urbana-Champaign, Illinois.

Amrith S. Gunasekara

Dr. Amrith Gunasekara works as a Research Scientist III with the State of California. He was the lead scientist working on greenhouse gases from agriculture at the California Department of Food and Agriculture. In that position, he coordinated and managed the California statewide research program on nitrous oxide emissions, sponsored jointly by the California Air Resources Board and California Energy Commission. Dr. Gunasekara received his Ph.D. from the University of California, Davis, in Agricultural and Environmental Chemistry. He has a B.S. in Environmental Sciences, a B.A. in Anthropology, and an M.S. in Plant and Soil Sciences from the University of Massachusetts, Amherst.

Laura L. McConnell

Dr. Laura McConnell is a Research Chemist at the U.S. Department of Agriculture, Agricultural Research Service (ARS) in Beltsville, Maryland. Dr. McConnell specializes in the investigation of processes controlling the movement of pesticides, volatile organic compounds and other pollutants from agricultural operations into the atmosphere or surface waters. Dr. McConnell is a past chair of the American Chemical Society, Division of Agrochemicals. She is currently Lead Scientist on an ARS project entitled, "Discerning the Fate of Atmospheric Agricultural Emissions in the Chesapeake Bay Region", and she has authored more than 75 peer-reviewed publications.

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

Subject Index

A

Abiotic production, 182
AD. *See* Anaerobic digestion (AD)
Africa, global nitrous oxide emissions, 266
Agricultural activities
  CH_4 emissions, 495*f*
  N_2O emissions, 495*f*
Agricultural burning, 276
  natural isotopic labeling, 284
Agricultural emissions, climate impacts
  biogenic aerosols, 289
  carbon isotopic measurements, 278
  organic reactivity and SOA, 280
  organics in precipitation, 286
  overview, 275
  primary combustion aerosols, 282
Agricultural Greenhouse Gas Accounting, 7
Agriculture
  emissions of nitrous oxide
    application of N fertilizer, 348
    cumulative flux, 351*f*
    denitrification, 346
    driving factors, 346
    effects of management, 348
    microbial process, 344, 345*f*
    nitrification, 345
    overview, 343
    possible mitigation options, 360
    response to climate change, 354
    source, 344
    weekly basis measurement, 350*f*
  single source of global N_2O, 165
  source of anthropogenic methane, 165
Agrobacterium tumerfaciens, 231
Agroecosystem
  agricultural management options for mitigating
    CH_4 emissions, 306*t*
    CO_2 emissions, 310*t*
    N_2O emissions, 304*t*
  assessing management alternatives, 312
  modeling approach, 312
  recommendations for field measurement, 326
AgrotainPlus, 17
Aircraft-mounted gas, 5
Alfalfa, 395
Alkaline-forming fertilizers, 183
Alkanes, 280
Alternative hydrogen sinks, 450
Ammonia, 51
  exchange fluxes, 59
  measurements, China, 54
Ammonia monooxygenase, 423
Ammonia oxidizing bacteria (AOB), 433
Anaerobic balloon, 315*f*
Anaerobic digestion (AD), 434
Angstrom's turbidity
  coefficient, 276
  formula, 276
Anhydrous ammonia (AA), 185
Animal agriculture, overview, 459
Animal manure
  composted, 509
  mitigate greenhouse gas emissions, 507
Animal-processed fibers (APF), 509
Animal proteins, 460
Anthropogenic pollutants, 281
AOB. *See* Ammonia oxidizing bacteria (AOB)
APF. *See* Animal-processed fibers (APF)
Asia, global nitrous oxide emissions, 266
Atmospheric aerosols, 276
  fraction of modern carbon, 279*t*
Automated chamber techniques, 167
Automated gas sampling system, 170*f*

B

Beef productivity, carbon footprint, 462
Berm, 233
Biochar, 214
  N_2O emissions, 215*f*, 216*f*
Bio-ethanol production, 268
Biogas, 508
Biogenic aerosols, climate impacts, 289
Biogenic hydrocarbons, 282
Biogeochemical cycles, chemical elements, 311*f*
Biomass
  energy content, 288*t*
  ulternative use, 286
Biorefinery technologies, 509
Black carbon (BC)
  absorption strengths, 290*f*
  aerosol, 291*f*
  levels measured at UALR, 283*f*
  major rain events, 289*f*
BNW. *See* Brigantine National Wildlife Refuge (BNW)

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

Bomb carbon, 278
Brigantine National Wildlife Refuge (BNW), 278
Brown carbon, 277
Buyers club, 468
Buying local, 460

C

Calcaric fluvisols, 109
California Department of Water Resources (CDWR), 227, 390
  distribution of agricultural land uses, 392*f*
California Energy Commission (CEC), 227
California Irrigation Meteorological Information System (CIMIS), 390
California rice system, 68
Calvin-Benson photosynthetic cycle, 284
Canadian Fertilizer Institute (CFI), 138
CAPRI-DNDC modelling framework (CDMF), 372
CAPRI-Spat Disaggregation Model, 374
Carbon dioxide, 300
Carbon footprint, 460
  average annual milk yield, 463*f*
  beef productivity reduces, 462
  exact number vs Delta, 466
  fuel use and carbon emissions, 468*f*
  improved dairy productivity reduces, 461
  link between efficiency, 460
  link between productivity, 460
  per kg of beef produced, 464*f*
  regional variation in dairy production, 462
  U.S. 1860 buffalo population and 2007 dairy industry, 463*f*
  variation, 467*f*
Carbon isotopic measurements, 278
  fine aerosols, 285*f*
Carbonaceous aerosols, 275, 282
Cattle production
  extensive, 412
  intensive, 413
  source of GHG, 408
CDMF. *See* CAPRI-DNDC modelling framework (CDMF)
CDWR. *See* California Department of Water Resources (CDWR)
CEC. *See* California Energy Commission (CEC)
CENTURY biogeochemical model, 355
CENTURY ecosystem model, 338
CENTURY model, 7, 205
CFC. *See* Chlorofluorocarbons (CFC)
CFI. *See* Canadian Fertilizer Institute (CFI)
Chamber methodology, soil, 4
  ground level, 5*f*
Chemical fertilizer, 96
CH_4 emissions
  chemical fertilizer, 96
  Chinese rice fields, 94
  cultivated rice, 127*f*
  estimation of rice fields, 98
  factors influencing, 94
  mitigation options for rice paddies, 110
  organic amendments, 94
  paddy rice fields, mitigation option, 168
    organic matter management, 170, 171*f*
    water management, 169
  temporal and spatial variations from rice fields, 96
  water management during rice-growing season, 95
  water status in preseason, 95
Chemodenitrification, 182
CH_4 fluxes
  different water regimes in the rice growing season, 171*f*
  field measurement techniques, 166
Chicken slaughter, 466
China, croplands
  consumption of chemical fertilizers, 92
  croplands, 92
  largest crop-producing, 92
  nitrous oxide emissions, 99
  prevent air pollution and increase soil fertility, 94
  rice cultivation, 96
  SOC storage, 108
  temporal variation in harvested areas, 93*f*
  three rice crops, 95
  variation in CH_4 fluxes from rice fields, 97
  various estimations of CH_4 emission, 99*f*
Chinese agro-ecosystem, 108
Chlorofluorocarbons (CFC), 473
CIMIS. *See* California Irrigation Meteorological Information System (CIMIS)
Clay loam soils, 45
COMET tool, 11
COMET-VR_2.0 – Decision Support System, 7
Common Agricultural Policy Regional Impact (CAPRI), 372
  input data, 372
  schematic representation, 373*f*

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

COMP. *See* Soil components layer (COMP)
Composting
  amendment of interest, 433
  anaerobic digestion, 434
  animal manures, 427
  animal mortalities, 433
  biological mechanisms of GHG production, 421
    denitrification, 424, 425*f*
    methanogens, 422, 425*f*
    nitrification, 423, 425*f*
  bulking agents, 432
  managing conditions, 429
  methanotrophic activity, 426
  soil C sequestration, 433
  soil fertility, chemical input, 433
  spatial profile of oxygen gradient, 428*f*
  summary of greenhouse gas emissions, 430*t*
  typical GHG emission patterns, 426
Compost turning strategy, 432
Condensed tannins, 449
Conservation tillage (CT), 203
Continuous corn (CT-CC) system, 17, 18
  average cumulative N_2O-N emissions, 20*f*
  cumulative daily N_2O-N emissions for each N source, 20*f*
  daily N_2O-N fluxes, 19*f*
Controlled release fertilizers (CRF), 193
Conventional cropping systems, 205
Conventional tillage (CT) systems, 352
Conventional till (CT) corn systems, 16
Corn-barley, 18
Corn-bean, 18
Cover crop, 353
CRF. *See* Controlled release fertilizers (CRF)
Crookston, MN
  2004 growing season results, 38
  2005 winter results, 41
  average wheat yield data and fertilizer N application rate, 43*f*
  experimental design and 2004 zoning map for fields, 40*f*
  on-farm investigation, 39
Crop evapotranspiration, 230
Cropland soils, organic C storage, 104
Cropping system, 17
  management, 137
    GHG emissions, 137
    global warming potential, 137
    N_2O emissions, 137
Crop residue, 354
C sequestration with crop residue incorporation, cropland in China, 323
CT. *See* Conservation tillage (CT); Conventional tillage (CT) systems
Cultivated rice, methane emission, 127*f*

D

Dairy farms
  emission factors, 498
  GHG model, 500
  greenhouse gas emissions
    mitigation of methane emissions, 503
    mitigation of nitrous oxide emissions, 505, 506*t*
    sources, 496, 497*f*
    strategies, 502
  methane and carbon dioxide, 496
  nitrous oxide, 496
  overview, 494
  quantification of GHG emission, 498
Dairy manure
  composted, 509
  energy and value-added products, 508*f*
DayCent model, 7, 338, 355
  biogeochemical model, flow diagram, 8*f*
DCD. *See* Dicyandiamide (DCD)
Decomposition, soil organic matter, 333
Denitrification, 30, 72, 204, 231, 424
  agriculture, emissions of nitrous oxide, 346
  arrhenius plot, 350*f*
  soil organic matter, 334
Denitrification decomposition model (DNDC), 205, 355, 374, 392
  agricultural management practices parameterized, 316*t*
  anaerobic balloon, 315*f*
  correlation of N_2O fluxes with nitrogen application, 395*f*
  data requirements and outputs, 389*f*
  data sources, 390
  greenhouse gas emissions for rice field, California in 1996, 322*t*
  list of agricultural land uses, cultivation areas, and N fertilizer application rates, 393*t*
  methodology, 389
  model scenarios, 391
  stimulated SOC, 325*f*
  uncertainties and limitations, 399
Denitrifier enzyme activity, 234
Denitrifying bacteria, 424
Di-ammonium phosphate, 183

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

Dicyandiamide (DCD), 151, 193
Dietary carbohydrates, types, 447
3,4-Dimethypyrazole phosphate (DMPP), 151, 152
Discerning agricultural management
  California: A case study, 206
  cover cropping on N_2O fluxes, 206
  methodology evaluation, 217
  microbial processes, 204
  overview, 203
  potential mitigation measures, 218
Dissolved organic carbon (DOC), 236, 286
  total amount of rain, 287*f*
Diurnal fluctuations, 210
  N_2O emissions, 212*f*
DMPP. *See* 3,4-Dimethypyrazole phosphate (DMPP)
DNDC. *See* Denitrification decomposition model (DNDC)
DNDC-CAPRI meta-model, 375
DNDC-EUROPE model, 374
DOC. *See* Dissolved organic carbon (DOC)
Drainage and emissions, 125
Drip irrigation, 245, 246*f*

E

Earth's climate, 473
EC. *See* Elemental carbon (EC)
ECC. *See* Encapsulated calcium carbide (ECC)
EEF. *See* Enhanced-efficiency fertilizers (EEF)
EF. *See* Emission factors (EF)
Eh. *See* Redox potential (Eh)
Elemental carbon (EC), 278
Emission factors (EF), 51, 344
Encapsulated calcium carbide (ECC), 194
Enhanced-efficiency fertilizers (EEF), 139
  use, 173
Enteric fermentation, 496
  emission factor of CH_4 from different animals, 498*t*
  mitigation of CH_4 emissions, 503, 504*t*
Environmental Protection Agency (EPA), 7, 414
EONR. *See* Optimum N rate (EONR)
EPA. *See* Environmental Protection Agency (EPA)
Ethical consumerism, 460
Europe, global nitrous oxide emissions, 257
European agricultural indicators, 375
Exact number *vs.* Delta, 466
Extensive cattle production, 412
Extensive systems, mitigation, 453

F

Feedlot beef production, 464
Feedlot cattle, 452
Fertilizer Institute, The (TFI), 138
Fertilizer management, 78
Fertilizer placement effects, on N transformations, 184
Fertilizer production, greenhouse gas emissions, 188
Fertilizer sources evaluated, 17
Field management, methane production, 76
Field measurement, recommendations, 326
Flood management, 81
Flux tower, measuring trace gas flux from plant-soil system, 6*f*
Food transport, 467
Fourier transform infrared spectroscopy (FTIR), 31
FTIR. *See* Fourier transform infrared spectroscopy (FTIR)

G

Gas samples, 33
Gaussian distributions, 238
  statistical parameters for fits of drip zone N_2O emissions, 240*t*
GDP. *See* Gross domestic product (GDP)
GEI. *See* Gross energy intake (GEI)
GHG. *See* Greenhouse gas (GHG)
GIS environmental database, 373
  input data, 373
Global CH_4 emission from paddy fields, mitigation potential, 172
Global nitrous oxide emissions
  accounting system, 262
  Africa, 267
  from agriculture divided by continent, 260*f*
  amount and intensity, 260
  anthropogenic sources, 258*f*
  Asia, 266
  capita emissions and projected growth rates, 261*t*
  costs, 263
  environmental conditions, 259
  Europe, 266
  fertiliser use and land areas in different regions, 261*t*

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

  food supply, 263
  growth rates in direct soil emissions, 259*f*
  meta-analysis of research studies, 258
  mitigation, 262
    different measures, 264*t*
    regional potential, 266
  North America, 267
  Oceana, 269
  overview, 257
  regional differences, 259
  relationship between direct soil, 262*f*
  South and Central America, 268
Global population, 263
Global positioning system (GPS), 35
Global warming potential (GWP), 4, 121, 122, 188, 344, 388, 444
  drainage and emissions, 125
  integration of rice yield and reducing rice fields, 127
  N fertilizer production, 189*t*
  overview, 121
  redox window with soil, 122
GNP. *See* Gross national product (GNP)
GPS. *See* Global positioning system (GPS)
Grazing, 351
Greenhouse gas emissions
  accounting methodologies, 335
  agriculture and forestry, 227
  associated with fertilizer production, 188
  croplands in China, 92, 103
  life cycle analysis approach, 193
Greenhouse gas (GHG), 16, 67, 135, 300
  agriculture's contributions, 136
  field experiments, 312
  measurements, 17
  rice culture, 67
  trends, 138*f*
Gross domestic product (GDP), 343
Gross energy intake (GEI), 413
Gross national product (GNP), 343
GWP. *See* Global warming potential (GWP)

H

Harber-Bosch process, 263
Hatch-Slack photosynthetic pathway, 284
Healthy redox, 125
Heterotrophic nitrification, 423
Homoacetogens ferment sugars, 71
Homogeneous Spatial Mapping Unit (HSMU), 373
HQ. *See* Hydroquinone (HQ)
HSMU. *See* Homogeneous Spatial Mapping Unit (HSMU)
Huang-Huai-Hai Plain of China, 107
HULIS. *See* Humic-like substances (HULIS)
Humic-like substances (HULIS), 275
Hydroquinone (HQ), 151

I

IDEAg. *See* Indicator Database for European Agriculture (IDEAg)
IFA. *See* International Fertilizer Industry Association (IFA)
Indicator Database for European Agriculture (IDEAg)
  applications, 377
  elements of the N-fluxes, 376*t*
  intensification of crop production, 378
  methods, 372
  nitrogen budget, 377
  overview, 371
  simulation of N_2O fluxes, 377
Inhibiting nitrification
  influence of urea granule size and inhibitors, 151
  potential, 152
Intensive cattle production, 413
Intensive systems, mitigation, 454
Intergovernmental Panel on Climate Change (IPCC), 6, 121, 331, 388
International Fertilizer Industry Association (IFA), 138
International Plant Nutrition Institute (IPNI), 138
Ionophores, 448
IPCC. *See* Intergovernmental Panel on Climate Change (IPCC)
IPCC tier comparison, soil carbon stock changes, 337
IPNI. *See* International Plant Nutrition Institute (IPNI)

K

Knowing your farmer, 460

L

Layer manure emissions, 483
LCA. *See* Life cycle analysis (LCA)

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

Leguminous crops, 354
Life cycle analysis (LCA), 462
Lipids, 449
Liquid fuels, 508
Livestock manure management, 419
  production from animals, 420
Local food, 460
Louisiana rice soil, 125

M

Manual chamber methods, 167
Manure
  anaerobic digestion for pretreatment, 434
  application, 351
  derived emissions, 453
  management, 409
    advantages and disadvantages, 421*t*
    emission factors of CH_4 and N_2O, 501*t*
    intensive cattle systems, 413
  storage mitigation of methane emissions, 503
Marginal emission factors (MEF), 360
Meatless Monday, 460
Mechanistic models, input parameters and processes, 502*f*
MEF. *See* Marginal emission factors (MEF)
Methane, 68
  biogenic sources, 69
  biogeochemistry, 71
  effect of temperature, 80
  elevated CO_2 effects, 80
  emissions from a rice field in Maxwell, California, 324*f*
  emmision, 72
    factors affecting rice systems, 74
  field management, 76
  global abundance, 68
  global sources and sinks, 70*t*
  mitigation potential, 77*t*
  redox zones and processes affecting rice, 72*f*
  relationship between rice, 75*f*
  soil characteristics, 76
  sources of organic matter, 73
Methane emissions
  chemical fertilizer, 96
  Chinese rice fields, 94
  cultivated rice, 127*f*
  estimation of rice fields, 98
  factors influencing, 94
  mitigation options for rice paddies, 110
  organic amendments, 94
  paddy rice fields, mitigation option, 168
    organic matter management, 170, 171*f*
    water management, 169
  temporal and spatial variations from rice fields, 96
  water management during rice-growing season, 95
  water status in preseason, 95
Methane oxidation, 334
Methane production, soil microenvironments, 130
Methanogenesis, 334
Methanogens, 71, 422
Methanotrophic bacteria, 423
Michaelis-Menten equation, 313
Microbial processes, nitrous oxide production from, 345*f*
Microbial survival, byproducts, 300
Microbiological processes contributing to soil, N_2O emissions, 231
Microbiological production, 181
Microirrigation systems, California perennial crops, 229
Microjet sprinkler, N_2O emissions distributions, 246*f*
Micrometeorological techniques, 167
Micro-sprinkler (MS) irrigation, 210
Midseason-drainage, 307
MITERRA-EUROPE model, 373
Mitigating CH_4 emissions, rice field in California, 321
Mitigating GHG emissions
  different stages of the environmental Eh evolution, 302*f*
  management options, 302
Mitigating N_2O emissions, crop field in Germany, 319, 320*f*
Mitigation
  extensive systems, 453
  intensive systems, 454
Mitigation options
  CH_4 emission from rice paddies, 110
  N_2O emission from croplands, 112
Moderate Resolution Imaging Spectroradiometer (MODIS), 282
MODIS. *See* Moderate Resolution Imaging Spectroradiometer (MODIS)
Monogastric animal productivity, 465
Monte Carlo simulations, 9
Most Sensitive Factor (MSF), 399
Mowing, 351
MS. *See* Micro-sprinkler (MS) irrigation
MSF. *See* Most Sensitive Factor (MSF)

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

N

NAEMS. *See* National Air Emissions Monitoring Study (NAEMS)
National Air Emissions Monitoring Study (NAEMS), 499
National Greenhouse Gas Inventory, 337
National Oceanic and Atmospheric Administration (NOAA), 390
Natural Resources Conservation Service, 390
NBPT. *See* N-(n-butyl) thiophosphoric triamide (NBPT)
N-containing inorganic salts, 185
NCP. *See* North China Plain (NCP)
Net primary production (NPP), 69, 333
NH_3 volatilization, 154
  rates, 155*f*
Nickels Soil Laboratory, 210
NIT. *See* Non-inversion-tillage (NIT)
Nitric acid, 349
Nitrification, 4, 30, 232, 345, 423
  earlier studies, 188
  heterotrophic pathway, 181
  microorganisms, 181
  rates, 183
  soil organic matter, 333
  soil plant system, 151
Nitrification inhibitor, 83, 139, 149
Nitrifier-denitrification, 181
Nitrite oxidizing bacteria (NOB), 433
Nitrobacter spp., 183
Nitrogen (N), 15
  application rates between barley and corn, 21
  check treatment in NT-CC system, 24*f*
  China, 52
  development of enhanced-efficiency, 16
  ecosystem, 349
  effectiveness, 24
  effects on soil pH and N transformations, 182
  management
    annual consumption, U.S., 137*f*
    4R nutrient stewardship, 138
    reasons for improving, 136
    source on cumulative N_2O-N emissions, 141*f*
  managing cropping systems, 15
  NT-CC system, 23*f*, 25*f*
  polymer-coated, 16
  production global warming potential, 189*t*
  relationship between grain, 352*f*
  source study, 22
  zoning map, 34*f*
Nitrogen oxide, 51
  exchange fluxes, 56
  flux variations, 60*f*
  measurements, China, 54
  origin, 60
Nitrogen use efficiency (NUE), 229
Nitrosomonas spp., 183
Nitrous oxide, 15, 51
  biogeochemistry, 71
  catabolic reactions, 29
  emissions in rice, 80
    cultivar influence, 83
    effect of flood management, 81
    fertilizer N impacts, 81, 82*f*
    organic matter application effects, 82
  exchange fluxes, 56
  flux variation, 56
  gaseous emission, 52
  global sources and sinks, 70*t*
  measurements, China, 54
  microbial production, 30
  mitigation potential, 77*t*
  origin, 60
  redox zones and processes affecting rice, 72*f*
  soil microorganisms, 69
  soil production, 29
Nitrous oxide emissions
  affected by water-filled pore space, 236*f*
  agricultural fields, mitigation option, 173
    optimizing fertilizer application rate, 173
    use of EEF, 173
  agricultural soil, 3
    coefficients of variation, 9
    comparisons of methods, 8
    complex models, 11
    fluxes, 5, 6*f*
    methods to quantify, 4
    overview, 3
    quantify soil surface, 6
    top down method, 5
    uncertainties, 8
  agriculture, 31
  background, 42
  biochar, 215*f*, 216*f*
  biogeochemical factors involved, 231
  California, spatial variability, 396, 398*f*
  California county, 395
  control, urea, and SuperU treatments during 2007 and 2008, 21*f*
  controlled release fertilizers in field experiments, 190*t*
  croplands, China, 99
    cropping systems, 100
    estimation of, 103

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

    - N fertilizer, 100, 101*f*
    - soil moisture and changes, 101
    - soil properties, 102
    - temporal and spatial variations, 102
    - typical seasonal pattern, 104*f*
  - cropping system studies, 18
  - data collected, 38, 44*f*
  - different N fertilizers in field experiments, 185, 186*t*
  - distribution of collars for gas flux chambers, 245*f*
  - diurnal fluctuations, 212*f*
  - DNDC simulated regional distribution, 397*f*
  - dryland production agriculture influences soil, 31
  - effect of nitrification inhibitors, 175*f*
  - fertigation events, 248*f*, 250*t*
  - as flux, 32
  - landscape scale variation contributing to soil, 236
  - measurement at soil surface, 30
  - meta-analysis measured, 193
  - microbiological processes contributing to soil, 231
  - N fertigation of urea nitrate, 212*f*
  - NP and SN plots during two maize growing periods, 56
  - NT-CB cropping system, 21*f*
  - NT-CDb cropping system, 22*f*
  - spatial variation in microbial activity, 233
  - spatiotemporal variation at vineyard scale, 238
  - St. Thomas, ND and Crookston, MN field, 45*f*
- Nitrous oxide mitigation, 10
- Nitrous oxide reductase (NOS), 231
- N-(n-butyl) thiophosphoric triamide (NBPT), 151
- NOAA. *See* National Oceanic and Atmospheric Administration (NOAA)
- NOB. *See* Nitrite oxidizing bacteria (NOB)
- N_2O fluxes, 166
  - cover cropping, 206
  - field measurement techniques, 166
  - irrigation and fertilization effects, 208
  - seasonal rates, 209*f*
- Non-inversion-tillage (NIT), 353
- N_2O production
  - geochemical and microbiological variables, 232*f*
  - pathways, 181
    - abiotic production, 182
    - kinetics, 182
    - microbiological production, 181
- North America, global nitrous oxide emissions, 267
- North China Plain (NCP), 51, 52
  - average fluxes and the crop yield from different plots, 57*t*
  - environmental implications, 61
  - sampling site, 53
- Northern California almond orchard, 210
  - cumulative emissions from a fertigation event, 213*f*
- NOS. *See* Nitrous oxide reductase (NOS)
- No-till continuous corn (NT-CC) system, 17
  - average cumulative N_2O-N emissions, 20*f*
  - cumulative daily N_2O-N emissions for each N source, 20*f*
  - daily N_2O-N fluxes, 19*f*
  - N rates, 25*f*
  - N source, 26*f*
- No-till (NT) corn systems, 16
- NPP. *See* Net primary production (NPP)
- NUE. *See* Nitrogen use efficiency (NUE)

O

- OC. *See* Organic carbon (OC)
- Oceana, global nitrous oxide emissions, 269
- Off-line monitoring systems, 167
- Oils, 449
- OM. *See* Organic matter (OM)
- On-line monitoring systems, 167, 168*f*
- Optimizing fertilizer application rate, 173
- Optimum N rate (EONR), 140
- Orchard scale, spatiotemporal variation in N_2O emissions, 244
- Organic amendments, 94
- Organic carbon (OC), 278
  - fraction of modern carbon, 279*t*
- Organic C storage
  - cropland soils, 105
    - changes, 107
    - factors, 109
- Organic matter (OM), 474
  - anaerobic degradation, 424*f*
  - management, 170
- *Oryza sativa*, 121
- Ozone, 51

P

- PAD. *See* Phosphoric acid diamide (PAD)

PCF. *See* Polymer-coated fertilizers (PCF)
Penmann-Monteith relationship, 244
Per unit of productive output, 408
Phosphoric acid diamide (PAD), 154
Planting density, 77
Polymer-coated fertilizers (PCF), 193
Polymer-coated urea, 16
Poultry litter fertilization
  animal manures, 479
  carbon dioxide emissions, 480
  commercial fertilizer, 478
  GHG emissions, 480
  methane emissions, 481
  nitrous oxide emissions, 483
  nutrient source in conservation agricultural systems, 475
  overview, 473
  plant macronutrients, 475
  soil carbon sequestration, 478
  subsurface band application, 482*f*
  surface broadcast application, 477*f*
Poultry production, U.S., 475
  broiler production, 476*f*
  turkey production, 476*f*
Prairie remnants, 42
Precipitation samples, 286
Precision feeding, 451
Primary combustion aerosols, 282
Process-based biogeochemical models, 388
Proteobacteria, 422
Pseudomonas aureofaciens, 231
Pseudomonas chlororaphis, 231
PU. *See* Urea prills (PU)
Pyrolyzed agricultural wastes, 203

Q

Quillaja saponaria, 449

R

Radiocarbon, measurement, 278
Reactive gaseous N species, 150
Redox potential (Eh), 122
  important reactions in soils, 124*t*
  minimum GWP contribution, 124*f*
Red River Valley of the North (RRV), 31
  map, 33*f*
Reducing CH_4 emissions, management practice, 303
Reducing CO_2 emissions, management practices, 307
Reducing N_2O emissions, management practice, 303
Reductive acetogenesis, 450
Residual nitrate, measurement, 140
Residue management, 214
Rice cultivars, 74
  influence, 83
Rice cultivation, 67
  flooding, 127
  global production, 68
  projected population, 71*f*
Rice field study, summary, 132*t*
Rice intensification, 79
Rice paddy
  sources of organic matter for methane production, 73
  spatial and physical characteristics, 73
Rice yield, effects of field management on CH_4 and N_2O emission, 130, 131*f*
Right N rate, 140
Right N source, 138
Right N time and place, 142
4R Nutrient Stewardship, 135
RRV. *See* Red River Valley of the North (RRV)
Rumen fermentation model, 447*f*

S

San Joaquin Valley Dairy Manure Technology Feasibility Assessment Panel, 508
Saponins, 449
S-benzylisothiouronium butanoate (SBT-butanoate), 194
S-benzylisothiouronium furoate (SBT-furoate), 194
SBT-butanoate. *See* S-benzylisothiouronium butanoate (SBT-butanoate)
SBT-furoate. *See* S-benzylisothiouronium furoate (SBT-furoate)
SD. *See* Surface drip (SD)
Seasonal N_2O emissions, 184
Secondary organic aerosols (SOA), 276
  organic reactivity, 280
Second National Soil Survey, 93
Senescence, 333
Sesbania rostrata, 78
Shimadzu DOC analyzer, 286
Shuangqiao farm, 52
SOA. *See* Secondary organic aerosols (SOA)
SOC. *See* Soil organic carbon (SOC)
Soil acidity, 182

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

Soil amendments, 214
Soil carbon stock changes
  IPCC tier comparison, 337
  U.S. croplands using IPCC Tier 1, 2 and 3 methods, 337*f*
Soil characteristics
  methane production, 76
Soil components layer (COMP), 390
Soil C sequestration, composting, 433
Soil fertility, 351
  composting, 433
Soil microbial activity, 332
Soil microcosm system with redox and pH control, 123*f*
Soil microenvironments, 130
Soil moisture, 346
  changes, 101
Soil nitrogen, 346
Soil organic carbon (SOC), 91, 214, 307, 474
  changes in cropland, 109
  content of croplands and non-croplands and coefficients of variation (CV), China, 107*t*
  dynamics in crop field in Heilongjiang Province, China, 323*t*
  dynamics of storage, 308*f*
  equilibrium level, 309*f*
  options, 113
Soil organic matter (SOM), 69
Soil organic matter (SOM) transformation
  cycling, 333
  decomposition, 331, 333
  denitrification, 334
  flow diagram of, 332*f*
  GHG accounting methodologies, 335
  IPCC default tier 1 methodology, 336*f*
  IPCC tier comparison, 337
  methanogenesis and methane oxidation, 334
  net primary productivity, 333
  nitrification, 334
  overview, 331
  senescence, 333
Soil percent water-filled pore space (%WFPS), 40
Soil properties, 102
Soil redox status, effect of field management, 128
Soils
  Eh profile under different treatments, 129*f*
  important microbial processes of N_2O, 344
  selected characteristics, 125*t*
  volume at each Eh range, 130*f*
Soil Survey Geographic database (SSURGO), 390
Soil temperature, 347
Soil water holding capacity (SWHC), 101
SOM. *See* Soil organic matter (SOM)
South and Central America, global nitrous oxide emissions, 268
Spikelet fertility, 80
SSD. *See* Sub-surface drip (SSD)
SSURGO. *See* Soil Survey Geographic database (SSURGO)
ST. *See* Standard tillage (ST)
St. Thomas, ND. Fields
  2003 growing season results, 36, 37*f*
  2004 growing season results, 38
  average potato yield data, 39*f*
  average wheat yield data, 37*f*
  on-farm investigation, 34, 34*f*, 35*f*
Standard tillage (ST), 203
  total seasonal N_2O emissions, 208*f*
Sub-surface drip (SSD), 210
  irrigation system, 213
SuperU, 17
Surface drip (SD), 210
Sustainability, 460
SWHC. *See* Soil water holding capacity (SWHC)
Synthetic fertilizers, 205

T

TFI. *See* Fertilizer Institute, The (TFI)
Tillage effects, 78, 206
Tillage system, 17, 352
  grain yields, cumulative N_2O-N emitted and emission factors, 355*t*
TMR. *See* Total mixed ration (TMR)
TNM. *See* Tonto National Monument (TNM)
Tonto National Monument (TNM), 278
Top down methods, 5
Total mixed ration (TMR), 409
Tower-based systems, 5

U

UALR. *See* University of Arkansas at Little Rock (UALR)
UAN. *See* Urea-ammonium nitrate (UAN) fertilizers
UAN-fertilized plots, 193
UC. *See* University of California (UC)

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

UCCE. *See* University of California Cooperative Extension (UCCE)
UNFCCC. *See* United Nations Framework Convention of Climate Change (UNFCCC)
United Nations Framework Convention of Climate Change (UNFCCC), 7, 335, 344
United States Environmental Protection Agency (USEPA), 388
University of Arkansas at Little Rock (UALR), 283*f*
  black carbon level, 283*f*
University of California Cooperative Extension (UCCE), 391
University of California (UC), 390
U placement method, 184
Urea
  forms in reducing reactive N species, 150
  granule size and inhibitors, 151
    impact, 154
  perspectives and progress, 150
  studies, 151
  super granule, 150
Urea-ammonium nitrate (UAN) fertilizers, 15, 16
Urea granule size and urease inhibitors
  decreasing NO_x emissions, 156, 157*f*
  minimizing NH_3 loss, 154
  reducing N_2O emissions, 158, 159*t*, 160*t*, 161*f*
Urea hydrolyzes, 183
Urea prills (PU), 150
Urease inhibitor, 154
Urine patches, 351
U.S. beef and dairy industries, 408
  greenhouse gas emissions sources
    carbon dioxide, 411
    effect, 411
    extensive cattle production, 412
    intensive cattle production, 413
  life cycle assessment, 414
  management, 408
  manure management, 409
  methane, 410
  nitrous oxide, 411
  overview, 408
U.S. beef and dairy production
  enteric emissions through
    dietary strategies, 446
    production efficiency, 451
  sources of greenhouse gases, 444
    methane, 444
    nitrous oxide, 445
  United States, 445
U.S. Central Great Plains, 15
U.S. Corn Belt, 474
U.S. cow-calf producers, 452
  manure-derived emissions, 453
U.S. dairy population, 461
U.S. Department of Agriculture (USDA), 390, 446
U.S. Environmental Protection Agency (USEPA), 499
U.S.A. soil GHG inventory, 338
USDA. *See* U.S. Department of Agriculture (USDA)
USEPA. *See* U.S. Environmental Protection Agency (USEPA)
U.S. National Greenhouse Gas Inventory, 7

V

VFA. *See* Volatile fatty acids (VFA)
Vineyard
  fertigation event, 242*f*, 243*f*
  soil denitrification potential, 234*f*
  spatial organization of, 233*f*
  spatiotemporal variation in N_2O emissions, 238
VOC. *See* Volatile organic compounds (VOC)
Volatile fatty acids (VFA), 412, 446
Volatile hydrocarbons, reaction rate with OH, 281*t*
Volatile organic compounds (VOC), 281

W

Water filled pore space (WFPS), 101, 232, 347
  N_2O emissions, 236*f*
Water management, 79, 169
  California perennial crops
    agricultural N_2O emissions, 228
    microirrigation systems, 229
    mitigation potential, 249
    overview, 228
  during rice-growing season, 95
Water status in preseason, 95
WFPS. *See* Water-filled pore space (WFPS)
%WFPS. *See* Soil percent water-filled pore space (%WFPS)
Wind velocity sensors, 5
Worldwide fertilizer consumption, 189*t*

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

Y

Yangtze River Delta (YRD), 51, 52
  NO_X and NH_3 fluxes from winter wheat and paddy field, 54, 55*f*
  sampling site, 52
Yellow River, 109
YRD. *See* Yangtze River Delta (YRD)
Yucca schidigera, 449

Downloaded by 89.163.35.42 on June 19, 2012 | http://pubs.acs.org
Publication Date (Web): October 11, 2011 | doi: 10.1021/bk-2011-1072.ix002

In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.